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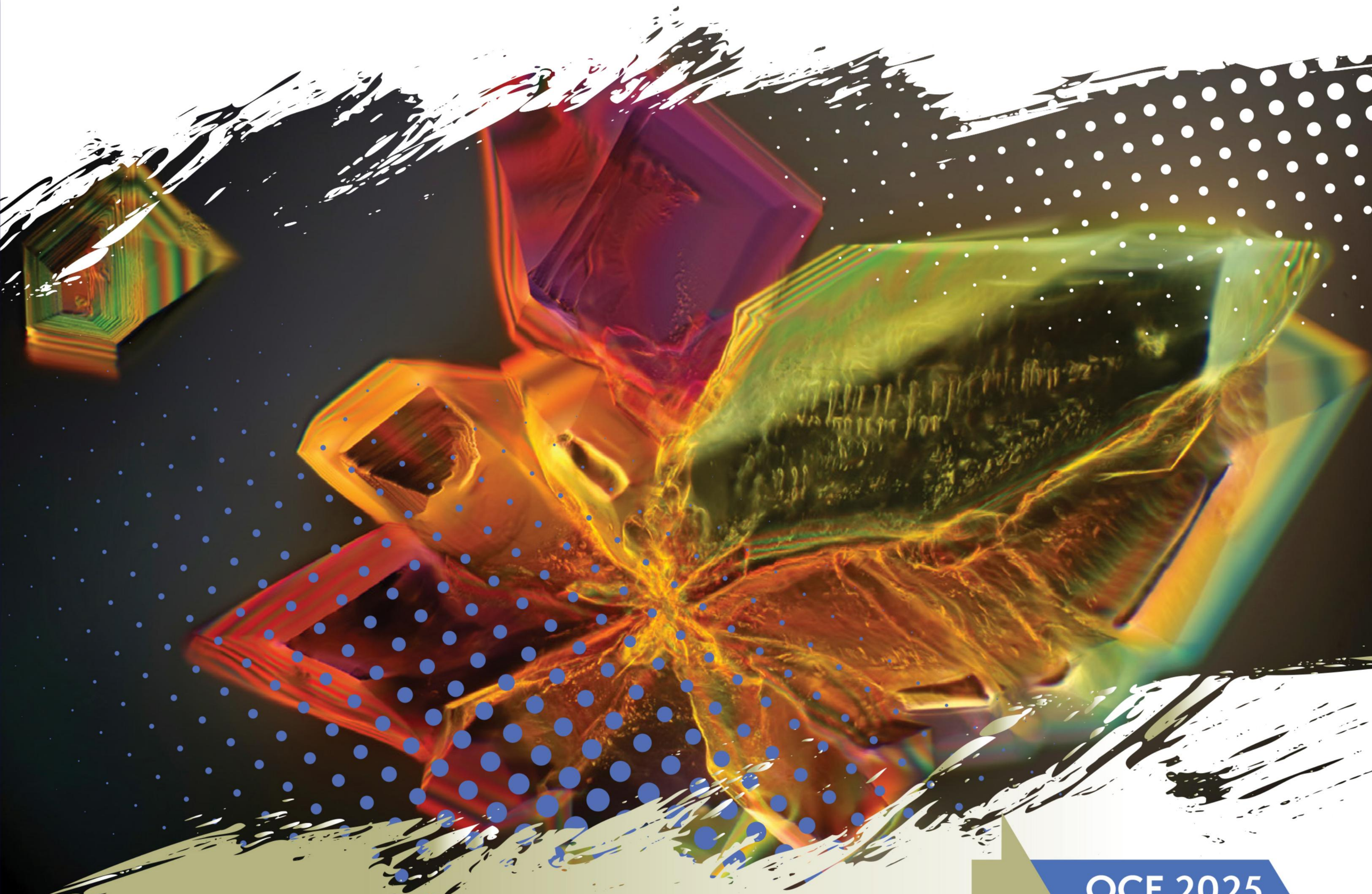

Student Book

QCE 2025 Chemistry

SYLLABUS

PEARSON

CHEMISTRY

2nd EDITION

QUEENSLAND

UNITS 3 & 4

STUDENT BOOK

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Syllabus
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This syllabus is still being refined in preparation for implementation in schools from 2025. For the most current syllabus versions and curriculum information, please refer to the QCAA website https://www.qcaa.qld.edu.au/.

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The CEA has established a tradition of providing up-to-date text, electronic material and support resources for both students and teachers, and professional development opportunities for teachers.

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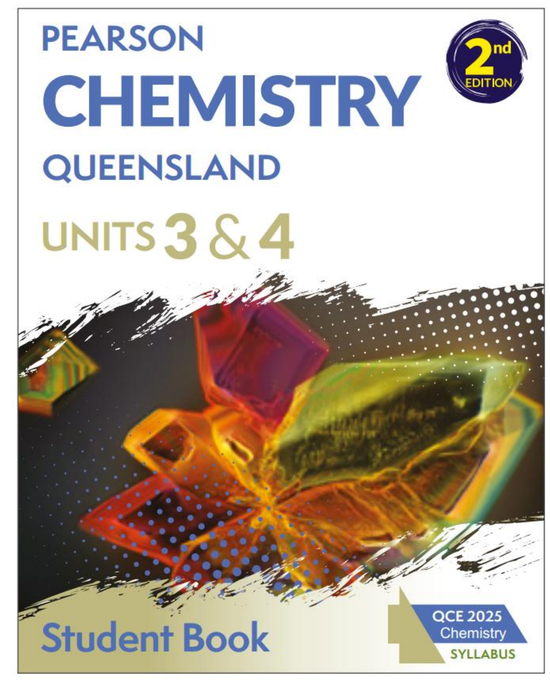

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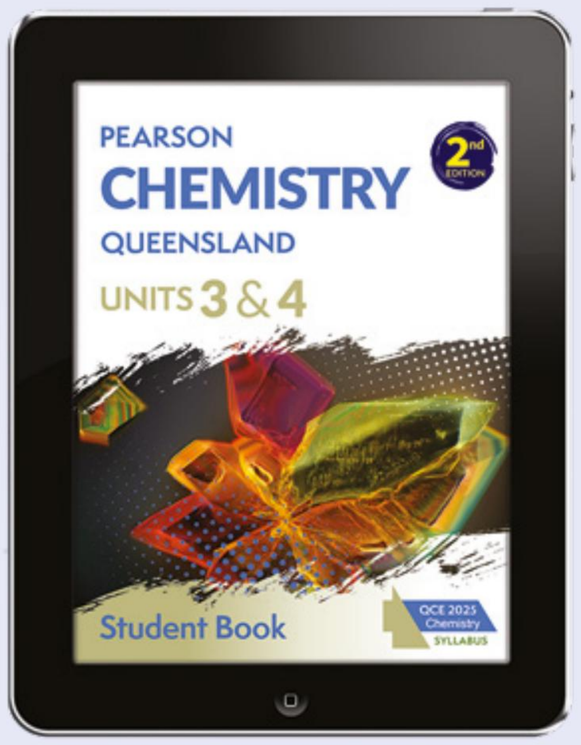

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How to use this book

PEARSON CHEMISTRY QUEENSLAND STUDENT BOOK UNITS 3 & 4 2ND EDITION

Pearson Chemistry Queensland Student Book Units 3 & 4 2nd edition has been written to the QCAA Chemistry 2025 Syllabus. This book includes an additional Skills and Assessment toolkit online as well as a depth of additional resources, to support every aspect of teaching and learning. Explore how to use this book below.

Design

Featuring best-practice literacy and instructional design, this series supports all learners with careful scaffolding of concepts and defined learning objectives.

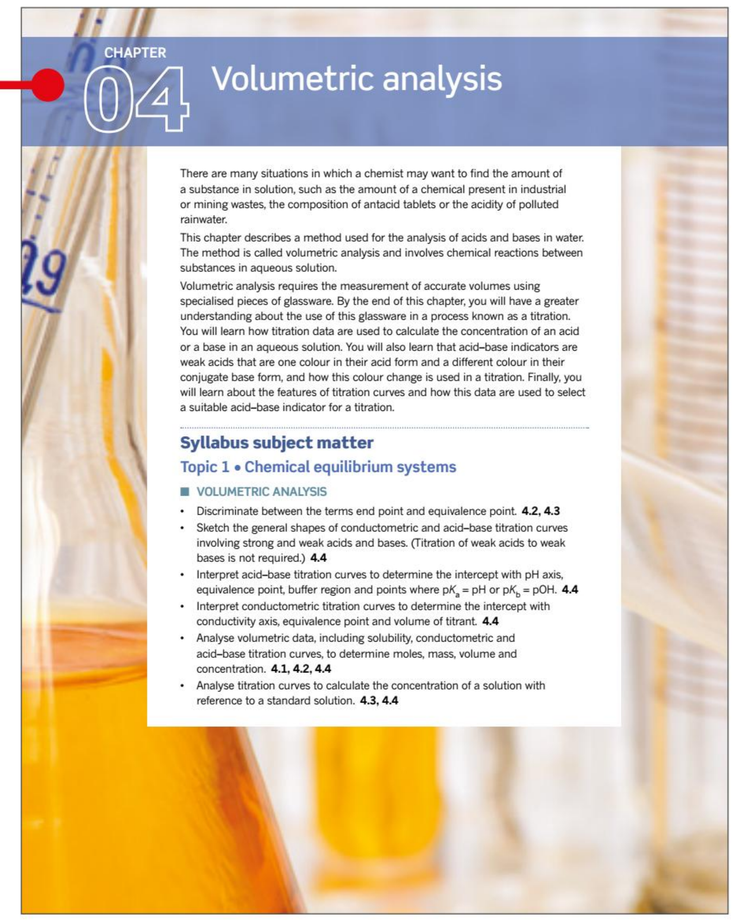
A simple-to-navigate, predictable design enables ease of use. The high-quality, relevant photos and illustrations assist student understanding of concepts.

Chemistry Skills and Assessment toolkit

The Skills and Assessment toolkit provides support across the science inquiry skills and assessment requirements. The material is presented as a handy reference to enable confident, complete coverage of the syllabus across the course. It has been reworked and fully updated to meet the evolved requirements of the revised QCAA Chemistry 2025 Syllabus and to respond to the needs of teachers and students.

Chapter openers

The syllabus subject matter addressed in each chapter is clearly listed and mapped to the modules in which the content is addressed.



CHAPTER 04 Volumetric analysis

There are many situations in which a chemist may want to find the amount of a substance in solution, such as the amount of a chemical present in industrial or mining wastes, the composition of antacid tablets or the acidity of polluted rainwater.

This chapter describes a method used for the analysis of acids and bases in water. The method is called volumetric analysis and involves chemical reactions between substances in aqueous solution.

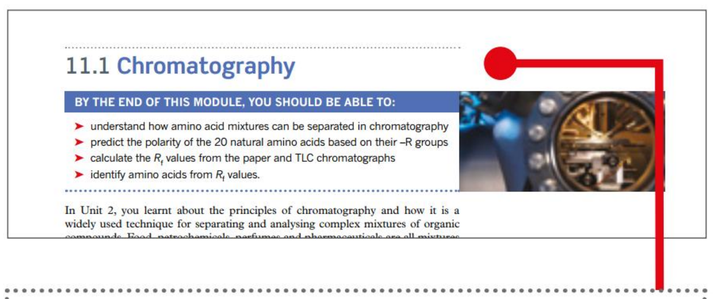
Volumetric analysis requires the measurement of accurate volumes using specialised pieces of glassware. By the end of this chapter, you will have a greater understanding about the use of this glassware in a process known as a titration. You will learn how titration data are used to calculate the concentration of an acid or a base in an aqueous solution. You will also learn that acid–base indicators are weak acids that are one colour in their acid form and a different colour in their conjugate base form, and how this colour change is used in a titration. Finally, you will learn about the features of titration curves and how this data are used to select a suitable acid–base indicator for a titration.

Syllabus subject matter

Topic 1 • Chemical equilibrium systems

VOLUMETRIC ANALYSIS

- Discriminate between the terms end point and equivalence point. **4.2, 4.3**
- Sketch the general shapes of conductometric and acid–base titration curves involving strong and weak acids and bases. (Titration of weak acids to weak bases is not required.) **4.4**
- Interpret acid–base titration curves to determine the intercept with pH axis, equivalence point, buffer region and points where pK_a = pH or pK_b = pOH. **4.4**
- Interpret conductometric titration curves to determine the intercept with conductivity axis, equivalence point and volume of titrant. **4.4**
- Analyse volumetric data, including solubility, conductometric and acid–base titration curves, to determine moles, mass, volume and concentration. **4.1, 4.2, 4.4**
- Analyse titration curves to calculate the concentration of a solution with reference to a standard solution. **4.3, 4.4**



11.1 Chromatography

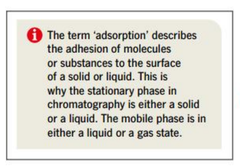
BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand how amino acid mixtures can be separated in chromatography
- predict the polarity of the 20 natural amino acids based on their –R groups
- calculate the R_f values from the paper and TLC chromatographs
- identify amino acids from R_f values.

In Unit 2, you learnt about the principles of chromatography and how it is a widely used technique for separating and analysing complex mixtures of organic

Module openers

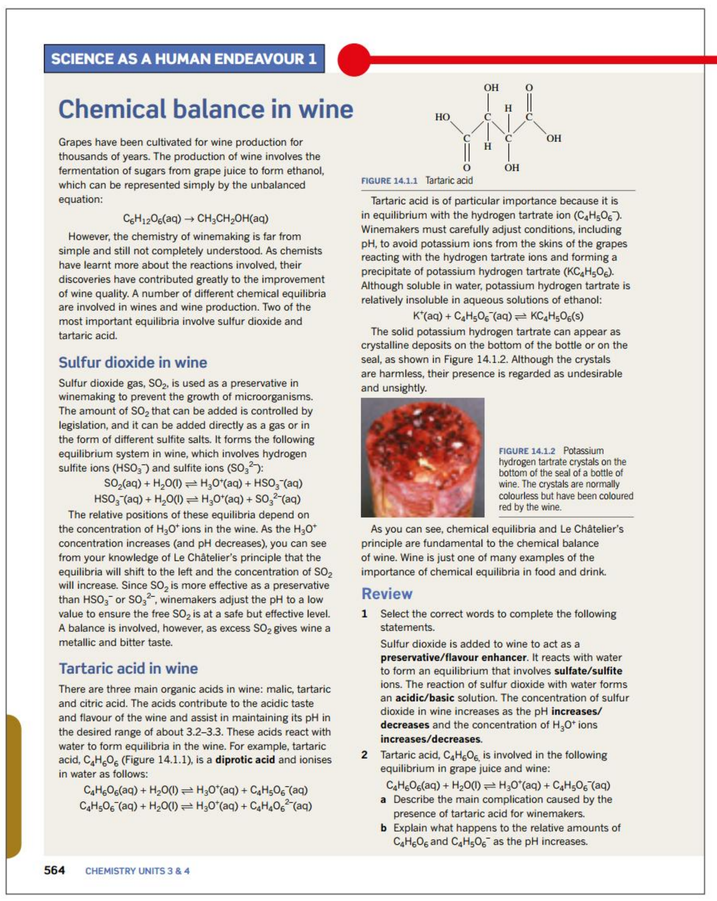
Module openers outline the key concepts and skills developed and link to syllabus subject matter listed in the chapter opener.



The term 'adsorption' describes the adhesion of molecules or substances to the surface of a solid or liquid. This is why the stationary phase in chromatography is either a solid or a liquid. The mobile phase is in either a liquid or a gas state.

Highlight boxes

Highlight boxes focus on important information such as key definitions, formulas and salient points.



SCIENCE AS A HUMAN ENDEAVOUR 1

Chemical balance in wine

Grapes have been cultivated for wine production for thousands of years. The production of wine involves the fermentation of sugars from grape juice to form ethanol, which can be represented simply by the unbalanced equation:

$$C_6H_{12}O_6(aq) \rightarrow CH_3CH_2OH(aq)$$

However, the chemistry of winemaking is far from simple and still not completely understood. As chemists have learnt more about the reactions involved, their discoveries have contributed greatly to the improvement of wine quality. A number of different chemical equilibria are involved in wines and wine production. Two of the most important equilibria involve sulfur dioxide and tartaric acid.

Sulfur dioxide in wine

Sulfur dioxide gas, SO_2, is used as a preservative in winemaking to prevent the growth of microorganisms. The amount of SO_2 that can be added is controlled by legislation, and it can be added directly as a gas or in the form of different sulfite salts. It forms the following equilibrium system in wine, which involves hydrogen sulfite ions (HSO_3^-) and sulfite ions (SO_3^{2-}):

$$SO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$$
$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_3^{2-}(aq)$$

The relative positions of these equilibria depend on the concentration of H_3O^+ ions in the wine. As the H_3O^+ concentration increases (and pH decreases), you can see from your knowledge of Le Châtelier's principle that the equilibria will shift to the left and the concentration of SO_2 will increase. Since SO_2 is more effective as a preservative than HSO_3^- or SO_3^{2-}, winemakers adjust the pH to a low value to ensure the free SO_2 is at a safe but effective level. A balance is involved, however, as excess SO_2 gives wine a metallic and bitter taste.

Tartaric acid in wine

There are three main organic acids in wine: malic, tartaric and citric acid. The acids contribute to the acidic taste and flavour of the wine and assist in maintaining its pH in the desired range of about 3.2–3.3. These acids react with water to form equilibria in the wine. For example, tartaric acid, $C_4H_6O_6$ (Figure 14.1.1), is a **diprotic acid** and ionises in water as follows:

$$C_4H_6O_6(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_4H_5O_6^-(aq)$$
$$C_4H_5O_6^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_4H_4O_6^{2-}(aq)$$

FIGURE 14.1.1 Tartaric acid

Tartaric acid is of particular importance because it is in equilibrium with the hydrogen tartrate ion ($C_4H_5O_6^-$). Winemakers must carefully adjust conditions, including pH, to avoid potassium ions from the skins of the grapes reacting with the hydrogen tartrate ions and forming a precipitate of potassium hydrogen tartrate ($KC_4H_5O_6$). Although soluble in water, potassium hydrogen tartrate is relatively insoluble in aqueous solutions of ethanol:

$$K^+(aq) + C_4H_5O_6^-(aq) \rightleftharpoons KC_4H_5O_6(s)$$

The solid potassium hydrogen tartrate can appear as crystalline deposits on the bottom of the bottle or on the seal, as shown in Figure 14.1.2. Although the crystals are harmless, their presence is regarded as undesirable and unsightly.

FIGURE 14.1.2 Potassium hydrogen tartrate crystals on the bottom of the seal of a bottle of wine. The crystals are normally colourless but have been coloured red by the wine.

As you can see, chemical equilibria and Le Châtelier's principle are fundamental to the chemical balance of wine. Wine is just one of many examples of the importance of chemical equilibria in food and drink.

Review

1 Select the correct words to complete the following statements.

Sulfur dioxide is added to wine to act as a **preservative/flavour enhancer**. It reacts with water to form an equilibrium that involves **sulfate/sulfite** ions. The reaction of sulfur dioxide with water forms an **acidic/basic** solution. The concentration of sulfur dioxide in wine increases as the pH **increases/decreases** and the concentration of H_3O^+ ions **increases/decreases**.

2 Tartaric acid, $C_4H_6O_6$, is involved in the following equilibrium in grape juice and wine:

$$C_4H_6O_6(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_4H_5O_6^-(aq)$$

a Describe the main complication caused by the presence of tartaric acid for winemakers.

b Explain what happens to the relative amounts of $C_4H_6O_6$ and $C_4H_5O_6^-$ as the pH increases.

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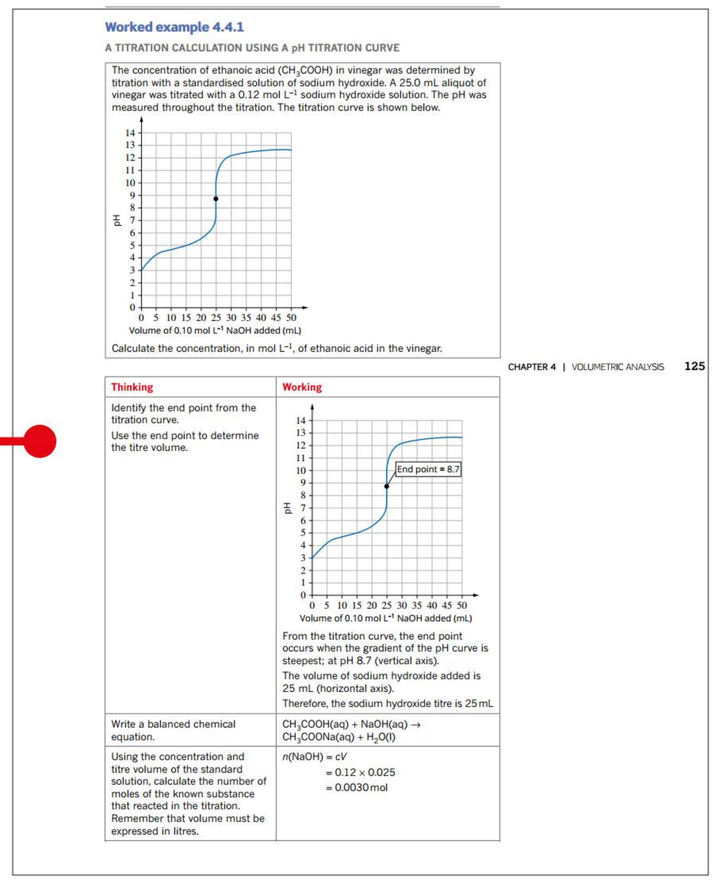
Science as a human endeavour

Science as a human endeavour (SHE) features provide stimulus for the research investigation. The SHE features are structured to develop the foundational skills relevant to supporting the relevant science inquiry skills through the lens of science as a human endeavour, providing a suitable foundation from which students can launch into research investigation IA3 and build proficiency for assessment objectives 1, 2 and 3.

Worked examples

Worked examples use sequential steps of thinking and working to model a best-practice approach to scaffolding student understanding of subject matter. This research-based approach greatly enhances student understanding and application of formulas to subject matter. Each Worked example is followed by a Try yourself task where students apply their learning to a mirrored problem to practise the skill.

Fully worked solutions to all Try yourself problems are available from *Pearson Chemistry Queensland Units 3 & 4 2nd edition eBook*.



Worked example 4.4.1

A TITRATION CALCULATION USING A pH TITRATION CURVE

The concentration of ethanoic acid (CH_3COOH) in vinegar was determined by titration with a standardised solution of sodium hydroxide. A 25.0 mL aliquot of vinegar was titrated with a 0.12 mol L^{-1} sodium hydroxide solution. The pH was measured throughout the titration. The titration curve is shown below.

Volume of 0.10 mol L^{-1} NaOH added (mL)

Calculate the concentration, in mol L^{-1}, of ethanoic acid in the vinegar.

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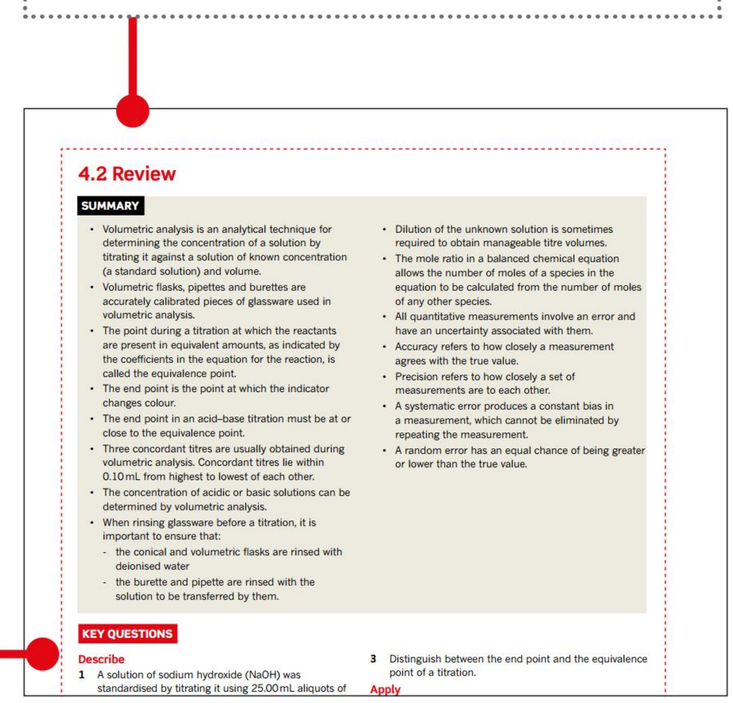
Thinking	Working
Identify the end point from the titration curve. Use the end point to determine the titre volume.	End point = 8.7. From the titration curve, the end point occurs when the gradient of the pH curve is steepest; at pH 8.7 (vertical axis). The volume of sodium hydroxide added is 25 mL (horizontal axis). Therefore, the sodium hydroxide titre is 25 mL
Write a balanced chemical equation.	$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$
Using the concentration and titre volume of the standard solution, calculate the number of moles of the known substance that reacted in the titration. Remember that volume must be expressed in litres.	$n(NaOH) = cV$ = 0.12 × 0.025 = 0.0030 mol

Module summaries

Each module concludes with a summary to help students consolidate the key points and concepts.



4.2 Review

SUMMARY

- Volumetric analysis is an analytical technique for determining the concentration of a solution by titrating it against a solution of known concentration (a standard solution) and volume.
- Volumetric flasks, pipettes and burettes are accurately calibrated pieces of glassware used in volumetric analysis.
- The point during a titration at which the reactants are present in equivalent amounts, as indicated by the coefficients in the equation for the reaction, is called the equivalence point.
- The end point is the point at which the indicator changes colour.
- The end point in an acid–base titration must be at or close to the equivalence point.
- Three concordant titres are usually obtained during volumetric analysis. Concordant titres lie within 0.10 mL from highest to lowest of each other.
- The concentration of acidic or basic solutions can be determined by volumetric analysis.
- When rinsing glassware before a titration, it is important to ensure that:
  - the conical and volumetric flasks are rinsed with deionised water
  - the burette and pipette are rinsed with the solution to be transferred by them.
- Dilution of the unknown solution is sometimes required to obtain manageable titre volumes.
- The mole ratio in a balanced chemical equation allows the number of moles of a species in the equation to be calculated from the number of moles of any other species.
- All quantitative measurements involve an error and have an uncertainty associated with them.
- Accuracy refers to how closely a measurement agrees with the true value.
- Precision refers to how closely a set of measurements are to each other.
- A systematic error produces a constant bias in a measurement, which cannot be eliminated by repeating the measurement.
- A random error has an equal chance of being greater or lower than the true value.

KEY QUESTIONS

Describe

1 A solution of sodium hydroxide (NaOH) was standardised by titrating it using 25.00 mL aliquots of

3 Distinguish between the end point and the equivalence point of a titration.

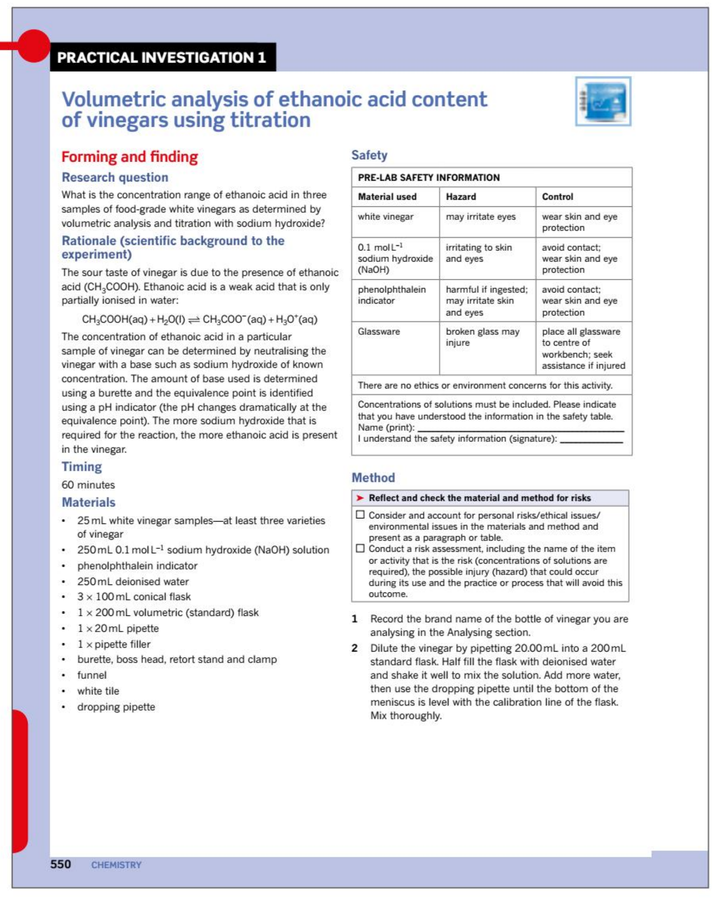
Apply

Module reviews

Key instructions are provided to test students' understanding of concepts covered in the module. Questions are presented under the four assessment objectives of Describe, Apply and Analyse. This structure allows students to demonstrate their progress in developing an understanding of the science subject matter.

Practical manual

Practical investigations offer students the opportunity to develop, practise and refine their science inquiry skills. These activities involve gathering primary data to analyse and respond to scaffolded or open-ended science tasks, supporting deeper understanding and proficiency in scientific methods. Additionally, these tasks allow teachers to formatively assess students' science inquiry skills and set students up well for student experiment IA2, pertinent to assessment objectives 1–6. All practical investigations have been trialled and tested to ensure they can be safely performed and yield effective results. Full risk assessments and additional support are provided in the eBook.



PRACTICAL INVESTIGATION 1

Volumetric analysis of ethanoic acid content of vinegars using titration

Forming and finding

Research question

What is the concentration range of ethanoic acid in three samples of food-grade white vinegars as determined by volumetric analysis and titration with sodium hydroxide?

Rationale (scientific background to the experiment)

The sour taste of vinegar is due to the presence of ethanoic acid (CH_3COOH). Ethanoic acid is a weak acid that is only partially ionised in water:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

The concentration of ethanoic acid in a particular sample of vinegar can be determined by neutralising the vinegar with a base such as sodium hydroxide of known concentration. The amount of base used is determined using a burette and the equivalence point is identified using a pH indicator (the pH changes dramatically at the equivalence point). The more sodium hydroxide that is required for the reaction, the more ethanoic acid is present in the vinegar.

Timing

60 minutes

Materials

- 25 mL white vinegar samples—at least three varieties of vinegar
- 250 mL 0.1 mol L^{-1} sodium hydroxide (NaOH) solution
- phenolphthalein indicator
- 250 mL deionised water
- 3 × 100 mL conical flask
- 1 × 200 mL volumetric (standard) flask
- 1 × 20 mL pipette
- 1 × pipette filler
- burette, boss head, retort stand and clamp
- funnel
- white tile
- dropping pipette

Safety

PRE-LAB SAFETY INFORMATION

Material used	Hazard	Control
white vinegar	may irritate eyes	wear skin and eye protection
0.1 mol L^{-1} sodium hydroxide (NaOH)	irritating to skin and eyes	avoid contact; wear skin and eye protection
phenolphthalein indicator	harmful if ingested; may irritate skin and eyes	avoid contact; wear skin and eye protection
Glassware	broken glass may injure	place all glassware to centre of workbench; seek assistance if injured

There are no ethics or environment concerns for this activity.

Concentrations of solutions must be included. Please indicate that you have understood the information in the safety table.
Name (print): _____
I understand the safety information (signature): _____

Method

➤ Reflect and check the material and method for risks

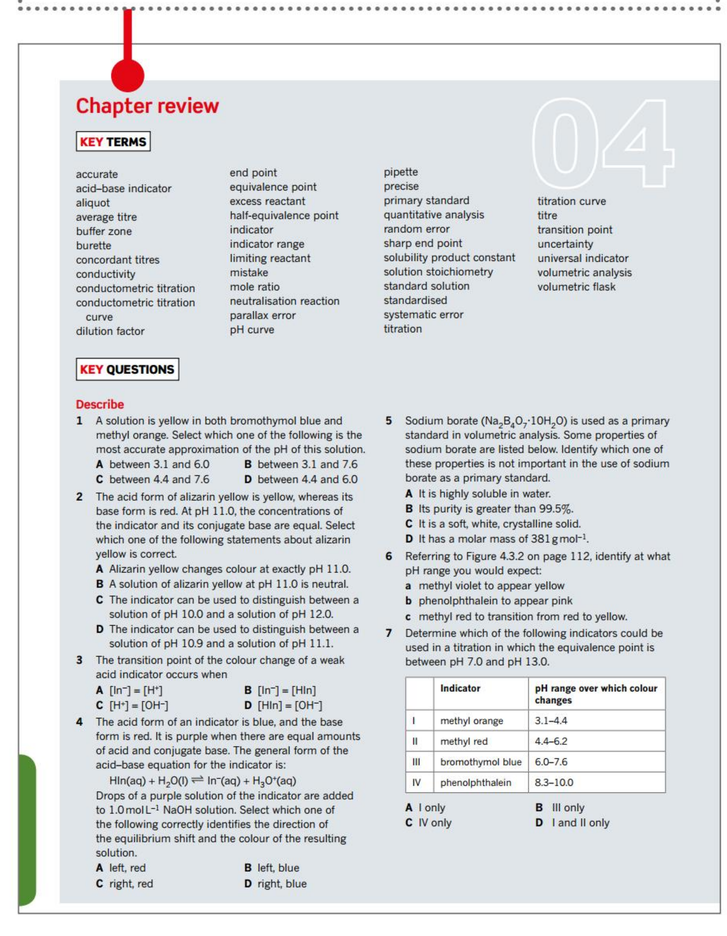
☐ Consider and account for personal risks/ethical issues/environmental issues in the materials and method and present as a paragraph or table.
☐ Conduct a risk assessment, including the name of the item or activity that is the risk (concentrations of solutions are required), the possible injury (hazard) that could occur during its use and the practice or process that will avoid this outcome.

1 Record the brand name of the bottle of vinegar you are analysing in the Analysing section.
2 Dilute the vinegar by pipetting 20.00 mL into a 200 mL standard flask. Half fill the flask with deionised water and shake it well to mix the solution. Add more water, then use the dropping pipette until the bottom of the meniscus is level with the calibration line of the flask. Mix thoroughly.

550 CHEMISTRY

Chapter reviews

Each chapter finishes with a list of key terms covered in the chapter and a set of multiple-choice and short-response questions, reflecting the style and experience of the external assessment (EA). These questions are organised under the four assessment objectives for the subject matter: Describe, Apply, Analyse and Interpret.



Chapter review 04

KEY TERMS

accurate, acid–base indicator, aliquot, average titre, buffer zone, burette, concordant titres, conductivity, conductometric titration, conductometric titration curve, dilution factor, end point, equivalence point, excess reactant, half-equivalence point, indicator, indicator range, limiting reactant, mistake, mole ratio, neutralisation reaction, parallax error, pH curve, pipette, precise, primary standard, quantitative analysis, random error, sharp end point, solubility product constant, solution stoichiometry, standard solution, standardised, systematic error, titration, titration curve, titre, transition point, uncertainty, universal indicator, volumetric analysis, volumetric flask

KEY QUESTIONS

Describe

1 A solution is yellow in both bromothymol blue and methyl orange. Select which one of the following is the most accurate approximation of the pH of this solution.
A between 3.1 and 6.0 B between 3.1 and 7.6
C between 4.4 and 7.6 D between 4.4 and 6.0

2 The acid form of alizarin yellow is yellow, whereas its base form is red. At pH 11.0, the concentrations of the indicator and its conjugate base are equal. Select which one of the following statements about alizarin yellow is correct.
A Alizarin yellow changes colour at exactly pH 11.0.
B A solution of alizarin yellow at pH 11.0 is neutral.
C The indicator can be used to distinguish between a solution of pH 10.0 and a solution of pH 12.0.
D The indicator can be used to distinguish between a solution of pH 10.9 and a solution of pH 11.1.

3 The transition point of the colour change of a weak acid indicator occurs when
A $[In^-] = [H^+]$ B $[In^-] = [HIn]$
C $[H^+] = [OH^-]$ D $[HIn] = [OH^-]$

4 The acid form of an indicator is blue, and the base form is red. It is purple when there are equal amounts of acid and conjugate base. The general form of the acid–base equation for the indicator is:
$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$
Drops of a purple solution of the indicator are added to 1.0 mol L^{-1} NaOH solution. Select which one of the following correctly identifies the direction of the equilibrium shift and the colour of the resulting solution.
A left, red B left, blue
C right, red D right, blue

5 Sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) is used as a primary standard in volumetric analysis. Some properties of sodium borate are listed below. Identify which one of these properties is not important in the use of sodium borate as a primary standard.
A It is highly soluble in water.
B Its purity is greater than 99.5%.
C It is a soft, white, crystalline solid.
D It has a molar mass of 381 g mol^{-1}.

6 Referring to Figure 4.3.2 on page 112, identify at what pH range you would expect:
a methyl violet to appear yellow
b phenolphthalein to appear pink
c methyl red to transition from red to yellow.

7 Determine which of the following indicators could be used in a titration in which the equivalence point is between pH 7.0 and pH 13.0.

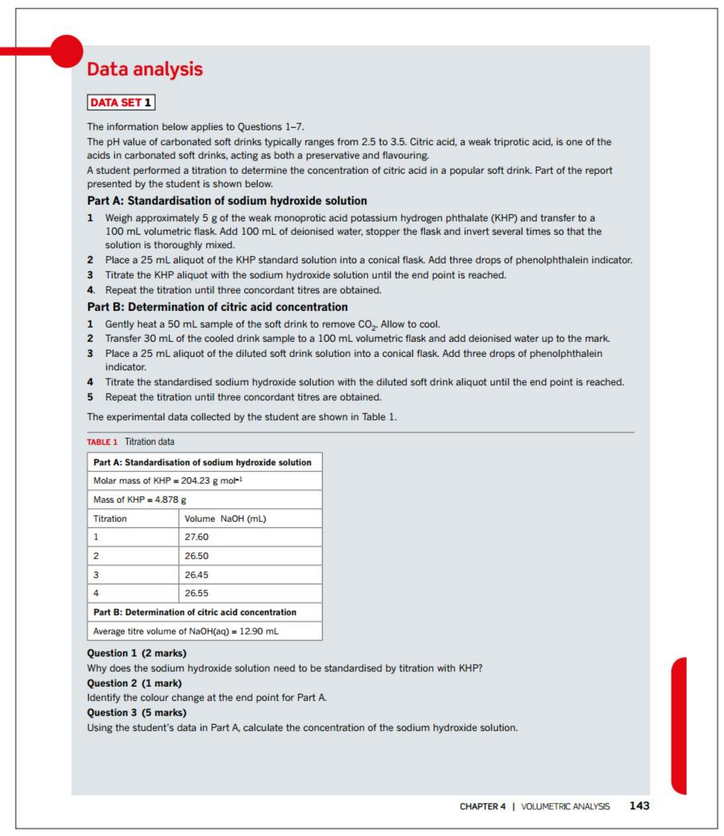
	Indicator	pH range over which colour changes
I	methyl orange	3.1–4.4
II	methyl red	4.4–6.2
III	bromothymol blue	6.0–7.6
IV	phenolphthalein	8.3–10.0

A I only B III only
C IV only D I and II only

How to use this book

Data analysis

Data analysis tasks at the end of each chapter review provide an opportunity to respond to questions that use a range of qualitative and quantitative data relevant to that subject matter. The data analysis tasks are structured to reflect the approach taken in the data test IA1 and align with the assessment objectives 2, 3 and 4.



Data analysis

DATA SET 1

The information below applies to Questions 1–7.
The pH value of carbonated soft drinks typically ranges from 2.5 to 3.5. Citric acid, a weak triprotic acid, is one of the acids in carbonated soft drinks, acting as both a preservative and flavouring.
A student performed a titration to determine the concentration of citric acid in a popular soft drink. Part of the report presented by the student is shown below.

Part A: Standardisation of sodium hydroxide solution

1 Weigh approximately 5 g of the weak monoprotic acid potassium hydrogen phthalate (KHP) and transfer to a 100 mL volumetric flask. Add 100 mL of deionised water, stopper the flask and invert several times so that the solution is thoroughly mixed.
2 Place a 25 mL aliquot of the KHP standard solution into a conical flask. Add three drops of phenolphthalein indicator.
3 Titrate the KHP aliquot with the sodium hydroxide solution until the end point is reached.
4. Repeat the titration until three concordant titres are obtained.

Part B: Determination of citric acid concentration

1 Gently heat a 50 mL sample of the soft drink to remove CO_2. Allow to cool.
2 Transfer 30 mL of the cooled drink sample to a 100 mL volumetric flask and add deionised water up to the mark.
3 Place a 25 mL aliquot of the diluted soft drink solution into a conical flask. Add three drops of phenolphthalein indicator.
4 Titrate the standardised sodium hydroxide solution with the diluted soft drink aliquot until the end point is reached.
5 Repeat the titration until three concordant titres are obtained.

The experimental data collected by the student are shown in Table 1.

TABLE 1 Titration data

Part A: Standardisation of sodium hydroxide solution	
Molar mass of KHP = 204.23 g mol^{-1}	
Mass of KHP = 4.878 g	
Titration	Volume NaOH (mL)
1	27.60
2	26.50
3	26.45
4	26.55
Part B: Determination of citric acid concentration	
Average titre volume of NaOH(aq) = 12.90 mL	

Question 1 (2 marks)
Why does the sodium hydroxide solution need to be standardised by titration with KHP?
Question 2 (1 mark)
Identify the colour change at the end point for Part A.
Question 3 (5 marks)
Using the student's data in Part A, calculate the concentration of the sodium hydroxide solution.

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Icons

Go To icons make important links to relevant content within the student books in the course.

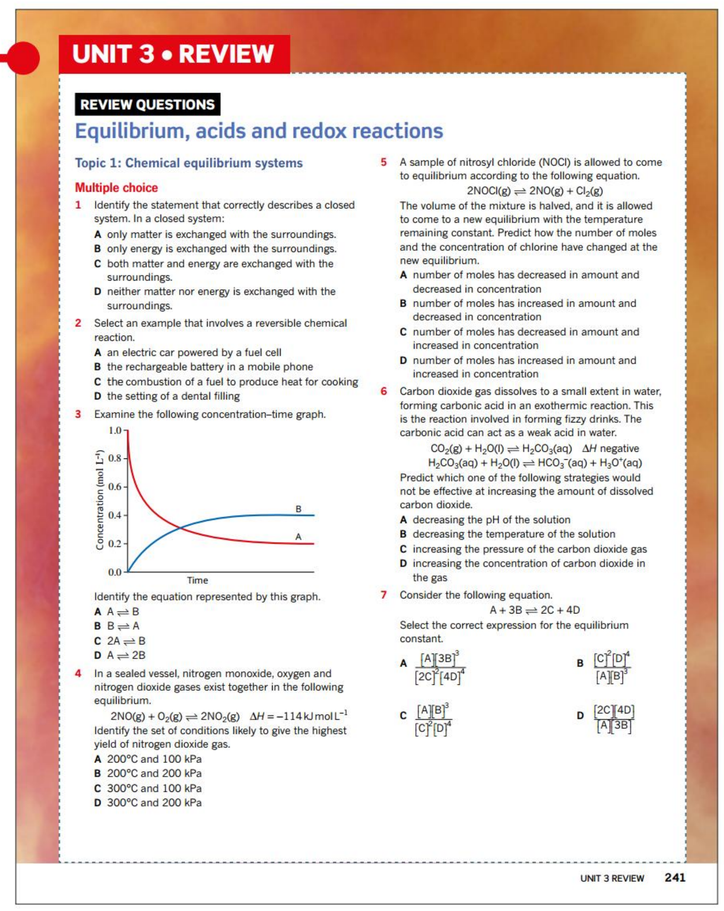
The Go To icons indicate:

- when a practical investigation would be suitable to engage with
- where support is available for skills and assessment tasks in Chapter 1 of your eBook.

Every practical investigation is supported by a complementary **SPARKlab** alternative practical.

Unit reviews

Each unit finishes with a comprehensive set of exam-style instructions, including multiple-choice and short-response questions in the style of the external assessment (EA). These review tasks assist students to draw together their science understanding of the subject matter of the whole unit.



UNIT 3 • REVIEW

REVIEW QUESTIONS

Equilibrium, acids and redox reactions

Topic 1: Chemical equilibrium systems

Multiple choice

1 Identify the statement that correctly describes a closed system. In a closed system:
A only matter is exchanged with the surroundings.
B only energy is exchanged with the surroundings.
C both matter and energy are exchanged with the surroundings.
D neither matter nor energy is exchanged with the surroundings.

2 Select an example that involves a reversible chemical reaction.
A an electric car powered by a fuel cell
B the rechargeable battery in a mobile phone
C the combustion of a fuel to produce heat for cooking
D the setting of a dental filling

3 Examine the following concentration–time graph.

Concentration (mol L^{-1}) 1.0, 0.8, 0.6, 0.4, 0.2, 0.0; Time; A; B

Identify the equation represented by this graph.
A A ⇌ B
B B ⇌ A
C 2A ⇌ B
D A ⇌ 2B

4 In a sealed vessel, nitrogen monoxide, oxygen and nitrogen dioxide gases exist together in the following equilibrium.
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = -114\ kJ\ mol\ L^{-1}$
Identify the set of conditions likely to give the highest yield of nitrogen dioxide gas.
A 200°C and 100 kPa
B 200°C and 200 kPa
C 300°C and 100 kPa
D 300°C and 200 kPa

5 A sample of nitrosyl chloride (NOCl) is allowed to come to equilibrium according to the following equation.
$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
The volume of the mixture is halved, and it is allowed to come to a new equilibrium with the temperature remaining constant. Predict how the number of moles and the concentration of chlorine have changed at the new equilibrium.
A number of moles has decreased in amount and decreased in concentration
B number of moles has increased in amount and decreased in concentration
C number of moles has decreased in amount and increased in concentration
D number of moles has increased in amount and increased in concentration

6 Carbon dioxide gas dissolves to a small extent in water, forming carbonic acid in an exothermic reaction. This is the reaction involved in forming fizzy drinks. The carbonic acid can act as a weak acid in water.
$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \quad \Delta H$ negative
$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$
Predict which one of the following strategies would not be effective at increasing the amount of dissolved carbon dioxide.
A decreasing the pH of the solution
B decreasing the temperature of the solution
C increasing the pressure of the carbon dioxide gas
D increasing the concentration of carbon dioxide in the gas

7 Consider the following equation.
$A + 3B \rightleftharpoons 2C + 4D$
Select the correct expression for the equilibrium constant.
A $\frac{[A][3B]^3}{[2C]^2[4D]^4}$
B $\frac{[C]^2[D]^4}{[A][B]^3}$
C $\frac{[A][B]^3}{[C]^2[D]^4}$
D $\frac{[2C]^2[4D]}{[A][3B]}$

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Glossary

Key terms are shown in **bold** throughout the Student Book and are listed at the end of each chapter. A comprehensive glossary at the end of the book defines all the key terms. The glossary aligns with the syllabus context and includes the QCAA defined terminology.

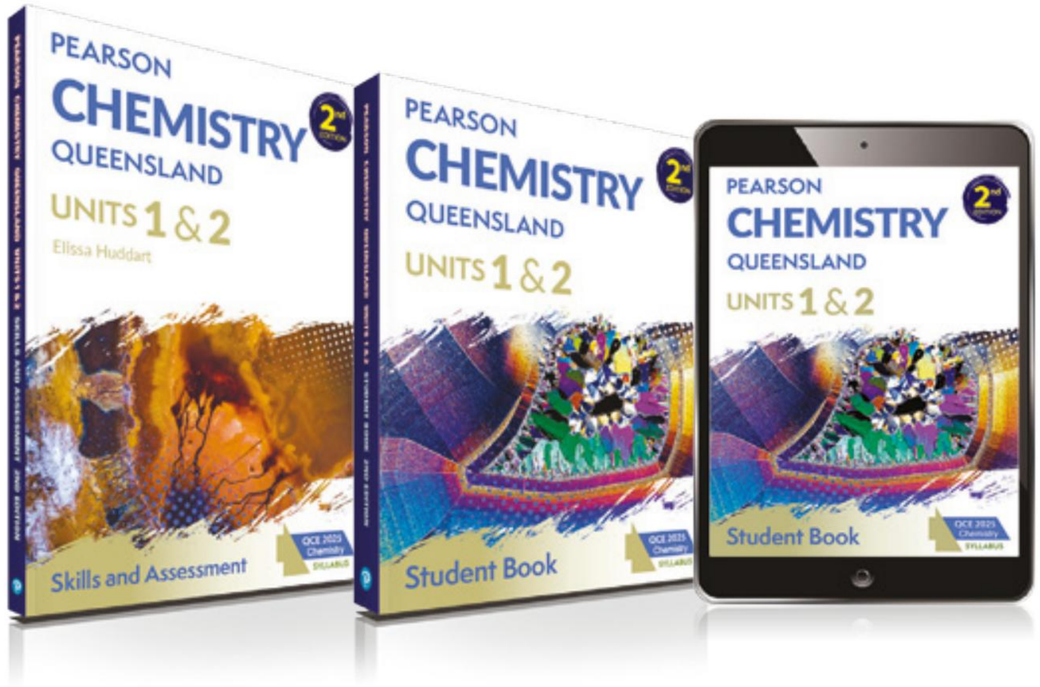
Answers

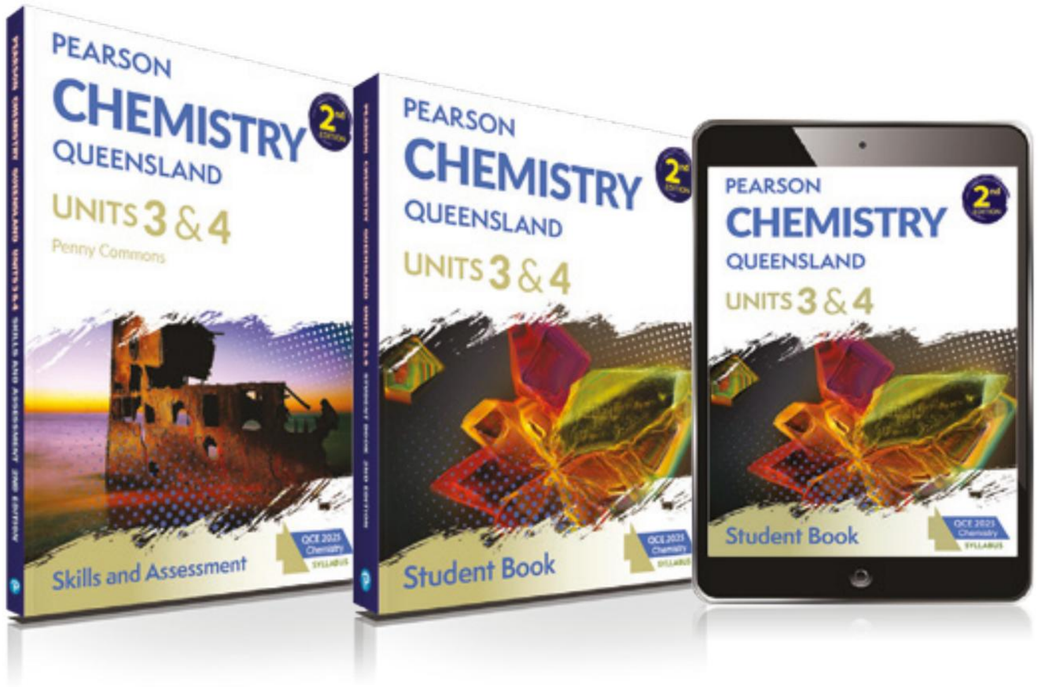
Comprehensive answers and fully worked solutions for all module reviews, Worked example: Try yourself, Science as a human endeavour, chapter review and unit review questions are provided via the eBook.

Pearson

Pearson Chemistry Queensland Units 3 & 4 2nd edition

Trusted throughout Queensland to provide high-quality support for the implementation of the QCAA Chemistry 2025 Syllabus, **Pearson Chemistry Queensland 2nd edition** has been refined to include what is needed to cover the QCAA outcomes.





Student Book

- The expert author team has delivered the same high-quality content you can trust, in the streamlined new edition for Queensland science classrooms.
- New, enhanced and updated features that make the new second-edition Student Books stand out:
  - New Science as a human endeavour sections
  - New data analysis tasks at the end of each chapter review
  - Enhanced and updated Skills and Assessment toolkit
  - Enhanced question sets
  - Updated Practical manual of practical investigations
  - Updated unit reviews and glossary.

Skills and Assessment Book

- The Skills and Assessment Book gives students the edge in preparing for all forms of assessment.
- It has been updated and re ined to respond to the revised syllabus and to specifically provide opportunities to consolidate, develop and apply subject matter and science inquiry skills. This resource features:
  - An updated toolkit
  - Key knowledge summaries
  - Worksheets
  - Practical investigations and guidance
  - Assessment practice
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CHAPTER

01 Chemistry Skills and Assessment Toolkit

This chapter provides important information and support in the study of the QCAA Chemistry General Senior Syllabus for Units 1 to 4.

The Chemistry Skills and Assessment Toolkit is designed to be used as a reference tool. It should be consulted on a need-to-know basis, where relevant, during this course of study. It is not intended that this chapter be worked through as a whole.

Focus

This chapter focuses on providing support and guidance in the following:

- **Developing and applying scientific skills**
  - Mathematical and statistical processes used in chemistry
  - SI units
  - Visual representations
  - Graphical representations
  - Measurement errors and uncertainty
- **Completing the assessment tasks**
  - Data test (Internal Assessment IA1)
    - Preparation in skill development
  - Student experiment (Internal Assessment IA2)
    - Forming a relevant research question
    - Justifying experiment modifications
    - Developing a methodology
    - Finding sufficient, relevant data
    - Interpreting and analysing evidence
    - Evaluating experimental process
    - Scientific writing and representations
    - Referencing sources
  - Research investigation (Internal Assessment IA3)
    - Developing a research question from a claim
    - Collecting relevant and sufficient evidence to answer a research question
    - Identifying and analysing trends, patterns, relationships in the evidence
    - Evaluating the quality and limitations of the evidence
    - Evaluating the research process
    - Scientific writing and representations
    - Referencing sources
  - Examination (External Assessment)
    - Understanding the features and conditions of the two exam papers
    - Applying strategies throughout the course to enhance learning
    - Applying strategies for revising and consolidating learning
    - Techniques and hints for sitting the exam

Chapter organisation

The chapter is arranged in four parts:

- Part A: Working scientifically
- Part B: Student experiment
- Part C: Research investigation
- Part D: Examination.

An outline of these parts is provided in the following pages.

QCAA Chemistry 2025 General Senior Syllabus objectives

The syllabus objectives require students to:

- describe ideas and findings
- apply understanding
- analyse data
- interpret evidence
- evaluate conclusions, claims and processes
- investigate phenomena.

Chemistry General Senior Syllabus 2025 © State of Queensland (QCAA) 2024.

Part A: Working scientifically

Part A focuses on basic mathematical skills and their applications. It features many worked examples and opportunities to apply these examples yourself. These skills are assessed, directly and indirectly, in assessment tasks and by analysing data in practical investigations.

Part A focuses on skills for the data test, and experiments. These skills are useful when completing sections of the student experiment, research investigation and the examination.

Refer to the following outline of Part A: Working scientifically to learn, revise and practise the skills in the areas in which you need help.

Module	Look here for	eBook page
1.1 Chemical science	- areas of chemistry - the work of scientific research	e7
1.2 Orders of magnitude	- scientific notation - transforming decimal notations to scientific notation - converting between scientific notation and scientific units, orders of magnitude and prefixes - SI prefixes - examples of calculations	e12
1.3 Mathematical basics for chemistry	- examples of maths used in chemistry - analysing straight-line graphs	e18
1.4 Units	- measurement and units - correct use of unit symbols - SI units - unit conversions	e21
1.5 Measuring precision and accuracy using uncertainty and percentage error	- explanations of the terms: ‘uncertainty’, ‘error’ ‘accuracy’ and ‘precision’ - causes of errors - calculations with uncertainty and error bars - writing measurements with uncertainty and error values - writing measurements and calculations to the correct significant figure - determining the absolute uncertainty of a value - converting between absolute and percentage uncertainties - calculating a value along with the associated uncertainty - calculating percentage error	e24
1.6 Tables and graphing	- arranging and recording data in tables - converting data from tables to graphs - types of graphs—scatter plots, line graphs, bar and column graphs - outliers and how they are represented on graphs - representing missing data on graphs	e41
1.7 Data analysis	- calculating mean, median, mode and range - regression, linear regression, and coefficient of determination	e49
1.8 Scientific writing	- writing scientifically - developing scientific representations - maintaining a science journal - referencing sources - in-text citations - using AI in research and writing - plagiarism - referencing AI sources - multimodal presentations	e53

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Part B: Student experiment (IA2)

Part B focuses on the student experiment. This internal assessment task requires students to follow the full scientific method over an extended and defined period of time. Students develop their own research question to investigate, based on an identified experiment related to Unit 3 subject matter.

Part B supports you through all aspects of the student experiment. The QCAA objectives and instrument-specific marking guide (ISMG) for the assessment are explained.

Part B provides examples of how to **modify (extend**, **refine** or **redirect)** the initial experiment to write an experimental research question. Included is a step-by-step guide to evaluate the quality of your question and explanations of scientific methodology. Part B also covers data types, data collection and analysis of data to draw valid conclusions. It includes how to evaluate the quality of data, including its reliability and validity, and how to link these to improvements and extensions. Also provided is support in writing up your scientific report, covering writing conventions and referencing sources.

Refer to the following outline of Part B: Student experiment to learn, revise and practise your skills in the areas in which you need help.

Module	Look here for	eBook page
1.9 Forming	- establishing background information - developing a rationale - defining variables - developing the research question - evaluating the research question - justifying the question modification - putting it all together: sample report	e66
1.10 Finding	- determining the risk assessment - managing risk - considering environmental and ethical issues - collecting sufficient and relevant raw data - collecting data electronically - putting it all together: sample report	e77
1.11 Analysing	- presenting the data - processing data using mathematical techniques - identifying patterns, relationships, trends in data - interpreting results - identifying uncertainty and limitations in the evidence - putting it all together: sample report	e86
1.12 Interpreting and evaluating	- drawing a conclusion that is linked to research question - discussing reliability and validity - identifying improvements and extensions to the research - putting it all together: sample report	e91

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Part C: Research investigation (IA3)

Part C focuses on the research investigation. This internal assessment task requires students to gather secondary evidence on a research question. It is completed over an extended and defined period of time. Students develop their own research question to investigate, based on a claim related to Unit 4 subject matter.

Part C supports you through all aspects of the research investigation. The QCAA objectives and instrument-specific marking guide (ISMG) for the assessment are explained.

Part C assists with writing your research question. It considers examples of claims and how to analyse claims for context, and guides you in developing your own research question. You will be guided in writing a specific and relevant research question that encompasses a small sub-section of the claim and is linked to Chemistry syllabus concepts. You will consider the information on locating and evaluating suitable secondary sources for the research, including identifying errors and relationships in data and assessing validity. You will learn how to formulate a justified conclusion and describe improvements and extensions. There is support for writing your scientific report, including scientific writing style and the structure of the report.

Refer to the following outline of Part C to learn, revise and practise the skills in the areas in which you need help.

Module	Look here for	eBook page
1.13 Forming and finding	- understanding a claim - classifying elements in the claim - identifying variables, terms and concepts related to the claim - developing a research question - planning the research - refining a research question - locating sources - putting it all together: sample report	e97
1.14 Analysing	- collecting sufficient and relevant evidence - identifying trends, patterns and relationships in the evidence - assessing limitations of the evidence - putting it all together: sample report	e110
1.15 Interpreting	- assessing if the evidence justifies the claim - presenting an argument on whether the claim is justified - reaching a conclusion about the claim - putting it all together: sample report	e116
1.16 Evaluating	- evaluating the quality of the evidence - suggesting any extrapolations of the claim - suggesting any improvements/extensions to the investigation - putting it all together: sample report	e119

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Part D: Examination (external assessment)

Part D focuses on the examination, a summative external assessment. The examination requires students to complete two 90-minute papers containing multiple-choice and short-answer questions. Each paper covers the whole chemistry course relating to Units 3 and 4. The examination constitutes 50% of the total assessment for the course.

Refer to this section early in the year, not just in the weeks before the examination. Effective exam preparation needs ongoing consolidation of learning and revision of course material at regular intervals. Effective preparation begins with a sound understanding of the course and its requirements. It is also important that you know where you can go for support and what sort of support is available to you through the course.

The examination requires that you use skills and strategies that are not necessarily used in the student experiment and research investigation. The internal data test and external examination are similar in the strategies you should apply to complete them. There is possibly more anxiety felt by students regarding the examination, as it accounts for 50% of the total mark in Chemistry. However, good preparation will see you entering the exam with confidence.

Part D guides you through all aspects of preparation for the examination. Refer to it to get tips on strategies to help you consolidate your learning and for revision hints and suggestions. Before completing practice exams, read through the list of strategies to use during perusal (reading) and writing time. Apply these as you answer each practice paper. Be aware that past exam papers from 2020 to 2024 relate to the Senior Chemistry 2019 syllabus, so use your 2nd edition student book to identify topics and questions that are no longer relevant to the Chemistry 2025 General Senior Syllabus. Conversely, special attention needs to be paid to the revision of topics that are added to the 2025 syllabus. Revision questions for new topics are provided in the 2nd edition student book. Your teacher will also provide advice about the correct use of past exam papers.

Sitting the exam involves more than having an understanding of the subject matter and possessing scientific skills. It is also about exam technique, as this can boost your performance.

Refer to the following outline of Part D: Examination as needed throughout the year to learn about strategies and techniques to enhance your learning, revision and examination performance.

Module	Look here for	eBook page
1.17 Examination preparation	- overview of the two papers (duration, content, response items and equipment) - strategies for consolidating learning - strategies for revising and practising - strategies for sitting the exam	e128

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1.1 Chemical science

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that chemistry is the study of materials and their properties and structure
- appreciate that chemistry uses mathematics
- explain the difference between scientific models, theories, laws, principles and facts
- understand that chemistry uses natural laws, theories, models and principles to describe real phenomena
- appreciate that understanding the theories and models that describe and explain the structure and properties of chemicals will help you make predictions and understand chemical systems
- recall the major areas of chemistry
- explain how a vast number of professions use some aspect of chemistry
- appreciate that chemistry is a dynamic and evolving branch of science and helps to explain phenomena and solve problems encountered in an ever-changing world
- understand that science provides a systematic approach for comprehending the world.

Science is a human endeavour to understand the world and the known universe. It is one of many methods used to develop knowledge. This knowledge is continually refined and redefined. Science follows a **methodology** to observe, test, measure, analyse and evaluate natural **phenomena** in a way that humans can understand and that allows us to construct meaning. There is no single **scientific method**; however, science follows a cyclical process that includes observation of natural phenomena, questioning, hypothesising and predicting, experimentation and gathering **data**, refining and altering all previous elements, and theorising (Figure 1.1.1).

In the Chemistry course, you will develop an understanding of chemical systems, and how **models** of matter and energy transfers and transformations can be used to describe, explain and predict chemical structures, properties and reactions.

FIGURE 1.1.1 A schematic outlining the processes involved in the scientific method. The scientific method is more of a cyclical process than a linear one.

Today, all scientific disciplines are expanding into new frontiers. The number of divisions and fields in chemistry is ever-increasing, and the relationship between disciplines is becoming more intertwined.

Innovations today are crossing traditional barriers between technology, chemistry, physics and biology of the past 100 or so years.

AREAS OF CHEMISTRY

Chemistry has been traditionally divided into four major areas—organic, inorganic analytical and physical.

Organic chemistry deals with molecules formed predominantly from carbon, hydrogen, oxygen and nitrogen. The range and diversity of organic molecules is enormous—literally millions of molecules have been identified. Very long molecules can be made up of much smaller organic building blocks, forming polymers such as plastics, which have become so common over the past few decades. Because living organisms are primarily made up of organic molecules, organic chemistry forms the molecular foundation of the biological sciences and is intimately linked with pharmaceuticals and drug design.

Inorganic chemistry is the study of molecules composed of other elements and includes salts, metals, semiconductors and nanomaterials. Biologically important molecules such as vitamins, haemoglobin and chlorophyll contain metal atoms and organic sections.

Inorganic and organic chemistry often involve the design and synthesis of new materials with particular chemical and physical properties related to chemical reactivity, boiling point, strength, colour or magnetism.

Analytical chemistry involves the analysis and quantification of chemical components of a sample. This is increasingly important with regards to the quality of manufactured goods, and in monitoring pollutant concentrations in our air, water and food. Even very low amounts of substances such as mercury or dioxins can be harmful to human health or the environment. Therefore, detecting and quantifying the amounts of these pollutants presents an ongoing intellectual and technical challenge.

Physical chemistry is the area of study of the physical properties, energies and spectra of all types of molecules, and the rate of chemical reactions. Physical chemists typically use spectroscopic or computational methods to study molecules, surfaces and chemical reactions. Sophisticated experimental techniques are required to probe complex or fast chemical processes, such as those that occur during combustion or the reactions taking place in the atmosphere.

Although traditional divisions in chemistry are still of vital importance, most of the exciting current scientific research is interdisciplinary and involves collaboration with many other scientific and technical fields including physics, biology, pharmacology, materials science, environmental science and engineering, leading to developments in nanotechnology, materials, pharmaceutical chemistry and environmental research.

The role and work of a chemist

Those who study chemistry are typically known as chemists. However, as the world is changing, science, technology, engineering and mathematics (STEM) fields are integrating numerous disciplines into vocational roles. A recent report from a multinational business organisation indicates that jobs in as much as 75% of growing and future industries will require STEM qualifications.

A STEM qualification fosters skills in areas such as creativity and critical thinking, and is highly regarded in public and private businesses. According to this report, the safest future occupations are doctors, nurses and teachers. The Australian Government's chief scientist report states that of Australia's current STEM workforce, only 3.3% of STEM students graduated with a major in chemical sciences. There are numerous reports every year outlining that the majority of future professions will be STEM-related.

> **i** Advances in science and innovation have seen a significant increase in multiple scientific specialities and disciplines working together. When more than one discipline is required to solve a problem or develop an innovation, it is said to be transdisciplinary. Transdisciplinary approaches to scientific endeavours form the heart of STEM.

The Royal Australian Chemical Institute identifies the jobs shown in Table 1.1.1 as being directly related to a chemistry qualification, but there are many other jobs for which chemistry is a useful background subject.

TABLE 1.1.1 Jobs in chemistry

Job	Typical job description
analytical chemist	uses a diverse range of methods to investigate the chemical nature of substances, to identify and understand the substance and to determine how it behaves in different conditions
clinical biochemist	analyses and interprets data relating to patients' samples to assist with the investigation, diagnosis and treatment of diseases
forensic scientist	provides impartial scientific evidence for use in courts of law to support the prosecution or defence in criminal and civil investigations
research scientist (physical sciences)	studies non-living systems to increase our understanding of how the physical world works; disciplines include astronomy, chemistry, earth science, materials science, meteorology and physics
chemical development engineer	is involved in the development of industrial processes for the production of a diverse range of products, as well as in commodity and specialty chemicals
science writer	researches, writes and edits scientific news articles and features for business, trade and professional publications, specialist scientific and technical journals, and the general media
toxicologist	plans and carries out laboratory and field studies to identify, monitor and evaluate the impact of toxic materials and radiation on human and animal health, the environment, and the impact of future technology
process engineer	develops economical industrial processes to produce the huge range of products on which modern society depends, including food and drink, fuel, artificial fibres, pharmaceuticals, chemicals, plastics, toiletries, energy and clean water

Table 1.1.2 lists jobs where a chemistry degree would be useful.

TABLE 1.1.2 A degree in chemistry would be beneficial in these jobs.

Job	Typical role description
patent agent	A patent agent obtains and enforces intellectual property rights on behalf of either individual inventors or organisations. Patents are granted by the government and give inventors the right to prevent the commercial use of inventions by other parties for a limited period. Chemists can specialise in pharmaceutical patent law.
environmental consultant	An environmental consultant works on commercial or government contracts to address a variety of environmental issues for their clients. This work covers a wide range of disciplines such as the assessment of air, land and water contamination, environmental impact assessment, environmental audit, waste management, and the development of environmental policies and management systems.
secondary school teacher or university lecturer	In addition to teaching chemistry to students, lecturers, in particular, may also undertake academic or industry research and may be involved in school or departmental management.

A list of some of the careers related to chemistry can be seen in Figure 1.1.2. The levels shown indicate the amount of training required, with Level 4 being the highest.

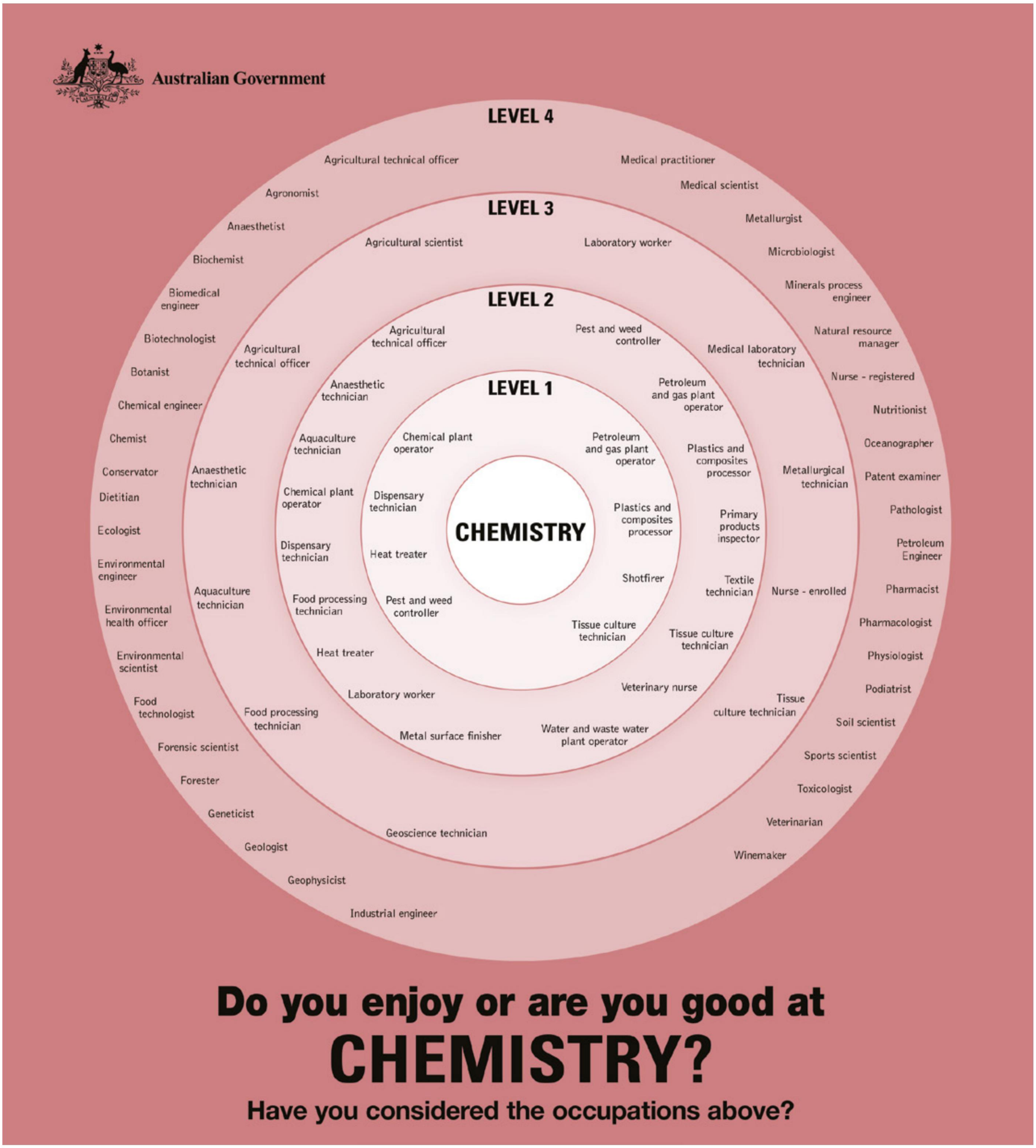


FIGURE 1.1.2 Examples of careers in fields related to chemistry

THE WORK OF SCIENTIFIC RESEARCH

The foundation of all sciences, including chemistry, is scientific research. Scientific research works in the unknown to develop new understandings. To build evidence, it may take years and many experiments. In interpreting scientific evidence, scientists endeavour to establish **models**, **theories**, **laws**, **principles** and **facts**. These change over time as knowledge develops, as illustrated in Figure 1.1.3.

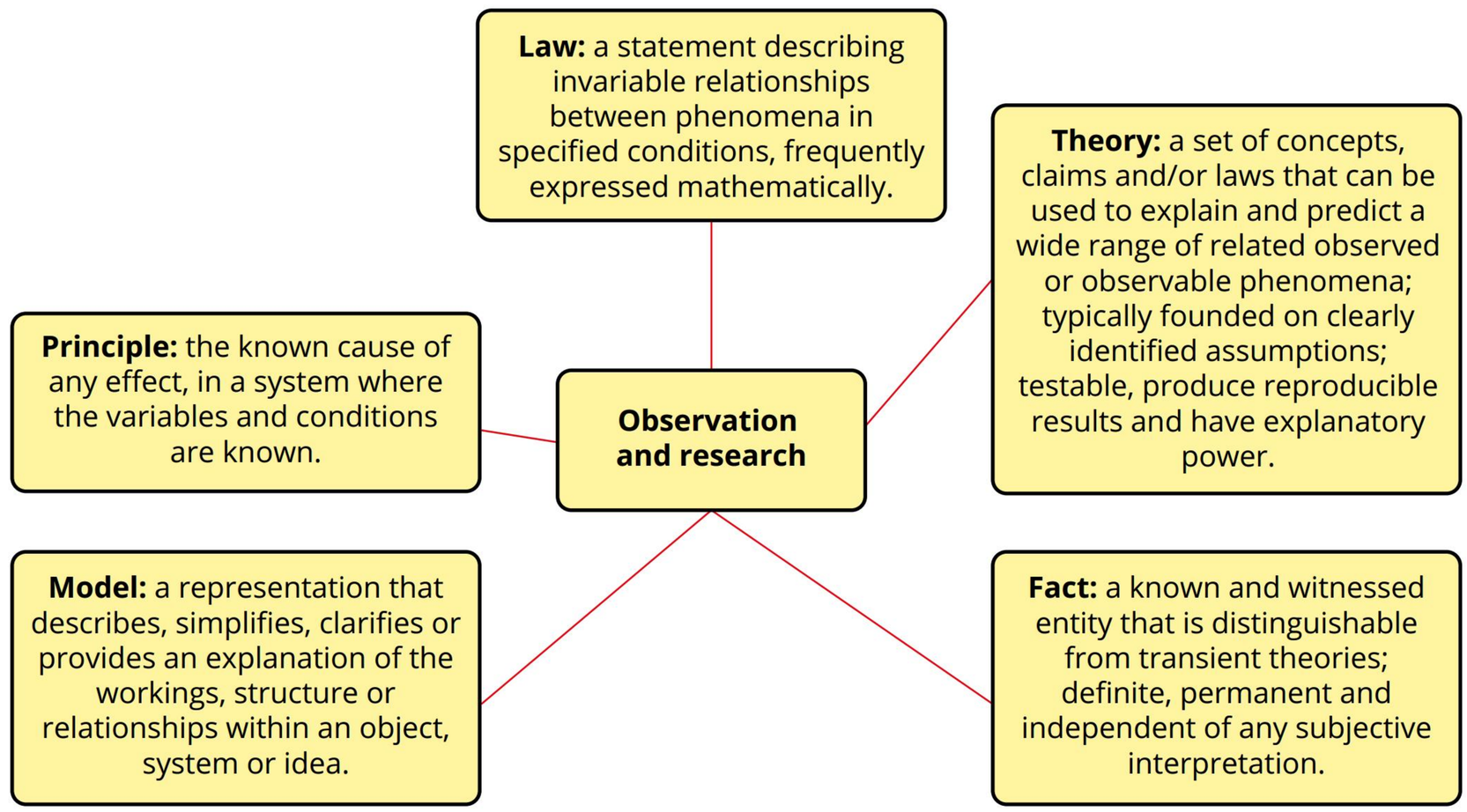


FIGURE 1.1.3 Scientific research and observations are used to establish or develop models, principles, laws, theories and facts.

1.1 Review

SUMMARY

- Science is a systematic approach to develop knowledge through testable explanations and repeatable means.
- Chemistry is the study of chemical systems, and how models of matter, energy transfer and transformations can be used to describe, explain and predict chemical reactions.
- There are four main areas of chemistry—organic, inorganic, physical and analytical.
- STEM (science, technology, engineering and mathematics) research is a transdisciplinary approach to scientific endeavours.
- Scientific evidence is used to formulate and establish models, theories, laws, principles and facts.
- A scientific model is a representation of a process, a phenomenon or data.
- A scientific theory is a well-established understanding and conceptual explanation of phenomena based on a body of evidence.
- A scientific law is a statement that describes relationships between phenomena in specified conditions.
- A scientific principle is the known cause of any effect in a system where the variables and conditions are known.
- A scientific fact is something that is known and witnessed and is distinguishable from transient theories; facts are definite, permanent and independent of any subjective interpretation.

Part A will consider the basic mathematical and data skills and applications that will be required for the student experiment, research investigation, data test and practicals.

1.2 Orders of magnitude

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- convert numbers to and from scientific notation
- estimate the value of a quantity using its order of magnitude
- recognise common SI prefixes.

SCIENTIFIC NOTATION

In scientific research and literature, measurements are often written in **scientific notation** to overcome confusion or ambiguity when displaying numbers with magnitude; for example, 2.56×10^{-6}. It is important to understand the numbers in scientific notation, their order of magnitude and how to convert them into other units.

Quantities are written as a number between one and ten, and then multiplied by an appropriate power of ten. Note that 'scientific notation', 'standard notation', 'standard form' and 'power of ten notation' all have the same meaning.

SKILLBUILDER 1.2.1

Transforming decimal notation to scientific notation

Scientists use scientific notation to handle very large and very small numbers. For example, instead of writing 0.000 000 035, scientists would write 3.5×10^{-8}.

A number in scientific notation is written as:

$a \times 10^n$

where:

- a is called the coefficient, and is a real number between 1 and 10; that is, $1 \leq a < 10$
- n is called the exponent, and is an integer (a positive or negative whole number). n is the power that 10 is raised to.

Note that if n is positive, then the number is greater than 1, and if n is negative, then the number is less than 1.

To transform a very large or very small number into scientific notation, perform the following steps.

1. Move the decimal place from its position in the original number until you get a number that is greater than or equal to 1 but less than 10.
2. Count the number of places that the decimal point has moved. This number is the exponent—the power of 10 (Figure 1.2.1).

- If the decimal point is moved n places to the left, n will be a positive number; for example, $510 = 5.1 \times 10^2$.
- If the decimal point is moved n places to the right, n will be a negative number; for example, $0.051 = 5.1 \times 10^{-2}$.

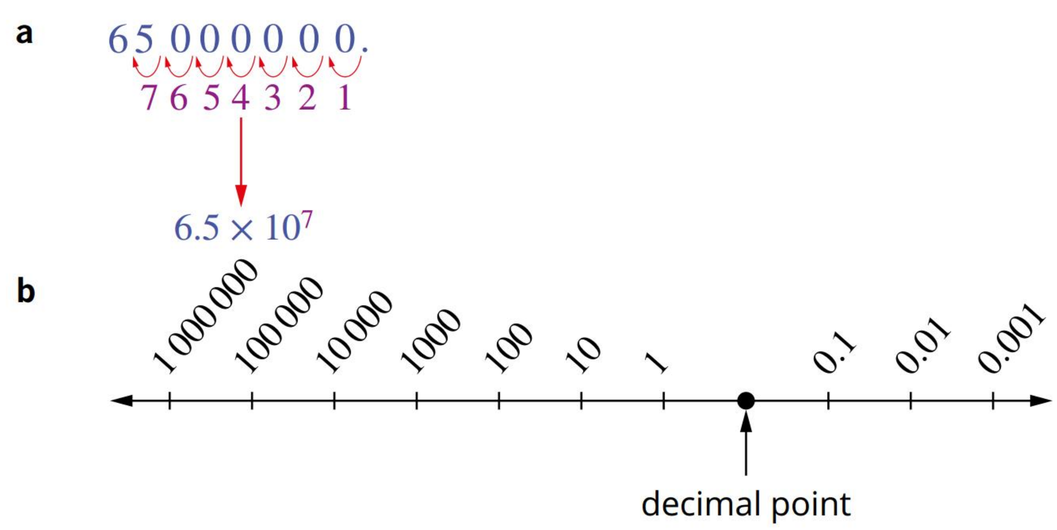


FIGURE 1.2.1 The value of the exponent is determined by counting the number of places the decimal point needs to be moved.

TABLE 1.2.1 Converting from scientific notation

Scientific notation	Number (expanded form)
1×10^{-9}	0.000 000 001
1×10^{-6}	0.000 001
1×10^{-3}	0.001
1×10^{-1}	0.1
1	1
1×10^{1}	10
1×10^{3}	1000
1×10^{6}	1 000 000
1×10^{9}	1 000 000 000

You will notice from Table 1.2.1 that when large numbers are written in scientific notation, the 10 has a positive exponent. Very small numbers smaller than 1 are written with 10 raised to a negative exponent.

Test the skill

Convert 121 000 to scientific notation.

Examples of some values written in scientific notation are:

- 6.02×10^{23} particles
- $25.25\,\text{mL} = 2.525 \times 10^{-2}\,\text{L}$
- $0.003\,02\,\text{mol} = 3.02 \times 10^{-3}\,\text{mol}$

Values given in scientific notation show the significant numbers and indicate the precision of measurement during experimentation by the instrument. Precision and accuracy are covered in more detail in Module 1.5.

Worked example 1.2.1

CONVERTING TO SCIENTIFIC NOTATION

The radius of a sodium atom is 0.000 000 000 160 m. How many individual sodium atoms can fit across a typical pin head with a diameter of 1.5 mm?

Thinking	Working
Calculate the diameter of a sodium atom (twice the radius).	0.000 000 000 320 m
Convert to scientific notation using the following steps.	—
Move the decimal place so that the number is represented as a number between 1 and 10.	0.000 000 000 320 → 3.20
Count the number of places the decimal place was moved.	10
Use the number of decimal places moved as the power exponent to base 10.	3.20×10^{10}
Determine whether the decimal was moved left or right.	right
Place a negative symbol (–) in front of the power of 10.	3.20×10^{-10} m
Convert 1.5 mm to m.	1.5 mm = 0.15 cm = 0.0015 m
Convert to scientific notation using the same steps as above.	1.5×10^{-3} m
Now calculate the number of individual sodium atoms that can fit on a pin head by dividing the pin head diameter (1.5×10^{-3} m) by the sodium atom diameter (3.20×10^{-10} m).	number of atoms $= \frac{1.5 \times 10^{-3}}{3.20 \times 10^{-10}}$ $= 4.7 \times 10^{6}$

➤ Try yourself 1.2.1

CONVERTING TO SCIENTIFIC NOTATION

The radius of a chloride ion is 0.000 000 000 181 m. Calculate how many chloride ions could fit across a pin head with a diameter of 1.5 mm.

You should be routinely using scientific notation to express very large and very small numbers. This also involves learning to use your calculator intelligently. Scientific and graphics calculators can be put into a mode whereby all numbers are displayed in scientific notation. It is useful when doing calculations to use this mode rather than frequently attempting to convert to scientific notation by counting digits on the calculator display.

An important reason for using scientific notation is that it removes ambiguity about the precision of some measurements. For example, a measurement recorded as 240 g could be a measurement to the nearest gram; that is, somewhere between 239.5 g and 240.5 g, or it could have been rounded up to the nearest 10 g. Writing this quantity as 2.40×10^{2} g makes the accuracy of the value clear (in this case, 3 significant figures).

Writing numbers using scientific notation

To write a number into long form from scientific notation, follow these rules.

- If the exponent is positive, write the coefficient without the decimal point. Continue to write zeros after the last digit in the coefficient until the number of digits after the first digit is equal to the exponent.
- If the exponent is negative, write a zero in the ones column, followed by a decimal point. Continue to write zeros until the total number of zeros (including the zero in the ones column) is equal to the positive value of the exponent. Then write the coefficient without the decimal place.

Worked example 1.2.2

WRITING QUANTITIES FROM SCIENTIFIC NOTATION

The mass of a neutron is 1.675×10^{-27} kg. Write this value in long form.

Thinking	Working
The exponent is negative, which means the number in long form is less than 1. Write a zero in the ones column and then a decimal point. After the decimal point, write another 26 zeros followed by the coefficient without the decimal place.	0.000 000 000 000 000 000 000 000 001 675 kg

➤ Try yourself 1.2.2

WRITING QUANTITIES FROM SCIENTIFIC NOTATION

Write the following values in long form.

a The diameter of a magnesium ion is 1.44×10^{-10} m.

b The number of hydrogen molecules in 1 mole of hydrogen gas is 6.02×10^{23}.

Scientific notation is the preferred way of communicating very large and very small numbers (such as measurements) in chemistry. Often for convenience and ease of use, quantities in chemistry problems should first be converted into scientific notation before any calculations can be carried out.

ORDERS OF MAGNITUDE AND PREFIXES

As stated above, scientists often work with very large or very small numbers in the measurements made during experimentation. These can be written using scientific notation or using a prefix before the unit to represent the order of magnitude. For example, a measurement of 2.56×10^{-6} m can be written as 256 μm. The symbol μ represents the prefix *micro* (Table 1.2.2), which means 'one millionth of the measured unit'. So, when *micro* is placed in front of metre, it becomes micrometre, meaning 'one millionth of a metre', therefore 256 μm becomes 256 millionths of a metre. An International System of Units (SI) **prefix** is a symbol written at the front of a unit to indicate that the measurement is a power of 10 higher or lower than the unit itself.

There are 20 SI prefixes in use, and most of them denote units that are one thousand (10^3) times larger or smaller than the previous prefix. Table 1.2.2 lists the SI prefixes commonly used in chemistry. You should become familiar with both scientific notation and prefixes for units of measurement. You should also be able to use them interchangeably.

TABLE 1.2.2 Common SI prefixes used in chemistry

Prefix	Symbol	Multiplier	Description	Decimal	Example
tera	T	10^{12}	trillion	1 000 000 000 000	Electricity generation provides over 20 000 terawatt-hours of energy a year.
giga	G	10^{9}	billion	1 000 000 000	Over 10 gigatonnes of carbon dioxide is produced from burning coal.
mega	M	10^{6}	million	1 000 000	1 MHz is close to the frequencies at which TV stations broadcast.
kilo	k	10^{3}	thousand	1000	1 kg is 1000 g.
hecto	h	10^{2}	hundred	100	1 hPa is a unit used in meteorology used to describe atmospheric pressure.
–	–	1	unit	1	–
deci	d	10^{-1}	tenth	0.1	A cube that holds 1 L has a capacity of 1 dm^3 (one cubic decimetre).
centi	c	10^{-2}	hundredth	0.01	1 cm is the same as 1/100th of a metre or 0.01 m.
milli	m	10^{-3}	thousandth	0.001	There are 1000 mm in 1 m.
micro	μ	10^{-6}	millionth	0.000 001	μg is commonly used as the unit for medicine dosage.
nano	n	10^{-9}	billionth	0.000 000 001	The wavelength of yellow sodium streetlights is 550 nm.
pico	p	10^{-12}	trillionth	0.000 000 000 001	The diameter of the hydrogen atom is about 100 pm.
femto	f	10^{-15}	quadrillionth	0.000 000 000 000 001	Some lasers emit a pulse of light that lasts for 1 fs.

Do not put spaces between the prefixes and the unit symbols. The larger prefixes are written as a capital letter, while the smaller prefixes are written using a lower-case letter. It is important to give a symbol the correct case (upper or lower case). There is a big difference between 1 mm and 1 Mm!

Note that the fundamental unit kilogram contains a prefix, but all multiples of mass are written with the base unit grams. As an example, one million kilograms is not written as one megakilogram, but as one gigagram (Gg).

Before any measurements with a prefix can be substituted into a formula, they must be converted into SI units without the prefix, i.e. written in scientific notation.

SI prefixes are used to avoid writing very small or very large numbers with lots of zeros. The prefix is added directly to the name of a unit, and a prefix symbol attaches directly to the symbol for a unit.

SKILLBUILDER 1.2.2

Converting between units

Often, in science, you may need to convert from one unit to another to complete a calculation. Knowing how to change between units is an important skill; however, conversion factors should be used carefully. As some units of measurement are difficult to visualise, knowing the size of different units in relation to each other will aid your understanding and help you avoid errors in your calculations. The most common mistake made with conversion factors is multiplying rather than dividing.

Cortisol is a natural hormone found in the body; however, it is used by some athletes to increase performance. Normal levels of cortisol in the blood are around 400 nmol L^{-1}. To put this into context, you can convert this value into a unit you can easily visualise, such as grams per litre (g L^{-1}).

To convert 400 nmol L^{-1} to mol L^{-1} (before converting to g L^{-1}), you need to move the decimal nine places to the left, so it becomes 0.000 000 4 mol L^{-1}.

This can also be written as 4.0×10^{-7} mol L^{-1}.

One mole of cortisol weighs 362.46 g; therefore, 0.000 000 4 mol L^{-1} is equal to 0.000 145 g L^{-1} (or 1.45×10^{-4} g L^{-1})—very small indeed!

Worked example 1.2.3

CONVERTING BETWEEN UNITS

Convert 60 700 grams to kilograms.	
Thinking	**Working**
To convert grams to kilograms, multiply 60 700 by kg per g. Since 1 kg = 1000 g, the kg is replaced by 1 and the g is replaced by 1000.	$= 60\,700 \times \frac{\text{kg}}{\text{g}}$ $= 60\,700 \times \frac{1}{1000}$ $= 60.7\,\text{kg}$

➤ Try yourself 1.2.3

CONVERTING BETWEEN UNITS

The rate of combustion of propane has been determined by measuring the production of CO_2 in mL. If CO_2 was generated at a rate of $25\,\mu\text{L}\,\text{s}^{-1}$, determine what this rate is in $\text{mL}\,\text{s}^{-1}$. Calculate how many litres of CO_2 would be produced in one hour.

When converting from one unit to another, it is essential that you check that the answer makes sense. For instance, if converting from μm to km, you would expect that there are many μm in a km. The inversion of prefix conversions is one of the major sources of mistakes in general chemistry.

1.2 Review

SUMMARY

- 'Scientific notation', 'standard notation', 'standard form' and 'power of 10 notation' all have the same meaning.
- A number in scientific notation is written as $a \times 10^n$, where:
  - a is called the coefficient, and is a real number between 1 and 10; that is, $1 \leq a < 10$
  - n is called the exponent, and is an integer (positive or negative).
- Prefixes are written in front of units to represent orders of magnitude.
- When converting units, it can be useful to write the conversions as fractions and then cross-cancel out to ensure that the conversion is done correctly.

KEY QUESTIONS

Describe

1 State why chemists need to write numbers in scientific notation instead of long form.

2 Identify the two numbers between which the coefficient of a number expressed in scientific notation has to lie.

3 State what the unit Tg means.

Apply

4 Represent the following values in scientific notation.

a 637 nm, expressed in m

b 319 s, expressed in s

5 Represent the following numbers in long form.

a 1.1×10^{-10} m

b 7.031×10^{6} m s^{-2}

6 Match each number with its scientific notation.

Number	Scientific notation
0.002	2×10^{3}
2000	1.234×10^{-1}
0.1234	2×10^{-3}
123.4	1.234×10^{1}
12.34	1.234×10^{2}

Analyse

7 Convert the following lengths into the unit in brackets, presenting the information in scientific notation.

a 1.56 mm (μm)

b 8.35 nm (cm)

8 A human hair is about 50 μm wide, whereas a virus is 2×10^{-8} m wide. How many times wider is the width of a human hair than the width of the virus?

1.3 Mathematical basics for chemistry

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that the rules of mathematics apply for solving mathematical operations or calculations in chemistry
- perform basic mathematical operations using percentages and fractions
- rearrange and substitute formulas using algebraic rules
- use the equation of a straight line to determine its gradient and *y*-intercept.

Science uses mathematics in working with data. The evidence can be quantified, measured and analysed. This is known as statistical analysis (a branch of mathematics).

When conducting mathematical operations or calculations, remember that all the rules of mathematics apply, including:

- order of operations
- rules for transposing formulas and working with fractions
- substitutions
- approximations.

EXAMPLES OF MATHEMATICAL BASICS FOR CHEMISTRY

Worked example 1.3.1 demonstrates examples of mathematics in chemistry.

Worked example 1.3.1

MATHEMATICAL BASICS IN CHEMISTRY

The rate of the reaction between two chemicals is given by the expression:

rate = $k[A][B]$

where k is the rate constant.

Determine the rate when $k = 2.503\ (\text{mol dm}^{-3})^{-1}\,\text{s}^{-1}$, $[A] = 0.100\,\text{mmol L}^{-1}$ and $[B] = 180.0\,\mu\text{mol dm}^{-3}$.

Thinking	Working
Convert the units and prefixes into SI units and scientific notation (if required).	$[A] = 1.00 \times 10^{-4}\,\text{mol dm}^{-3}$ $[B] = 180.0 \times 10^{-6}\,\text{mol dm}^{-3}$ (or $1.800 \times 10^{-4}\,\text{mol dm}^{-3}$)
Write down the equation.	rate = $k[A][B]$
Substitute in the values.	rate = $2.503 \times 1.00 \times 10^{-4} \times 1.800 \times 10^{-4}$ $= 4.5054 \times 10^{-8}\,\text{mol dm}^{-3}\,\text{s}^{-1}$
Express your answer to the lowest number of significant figures in the data.	rate = $4.51 \times 10^{-8}\,\text{mol dm}^{-3}\,\text{s}^{-1}$

➤ Try yourself 1.3.1

MATHEMATICAL BASICS IN CHEMISTRY

A hydrogen atom has a diameter of 64 pm. If the atom is represented as a sphere, calculate:

a the volume of a hydrogen atom

b the surface area of a hydrogen atom.

ANALYSING STRAIGHT LINES

A straight line is the simplest relationship between two variables. The **dependent variable** is plotted on the vertical or y-axis, and the **independent variable** is on the horizontal or x-axis. The relationship between the two variables is represented by the gradient. Figure 1.3.1 shows a typical straight-line relationship.

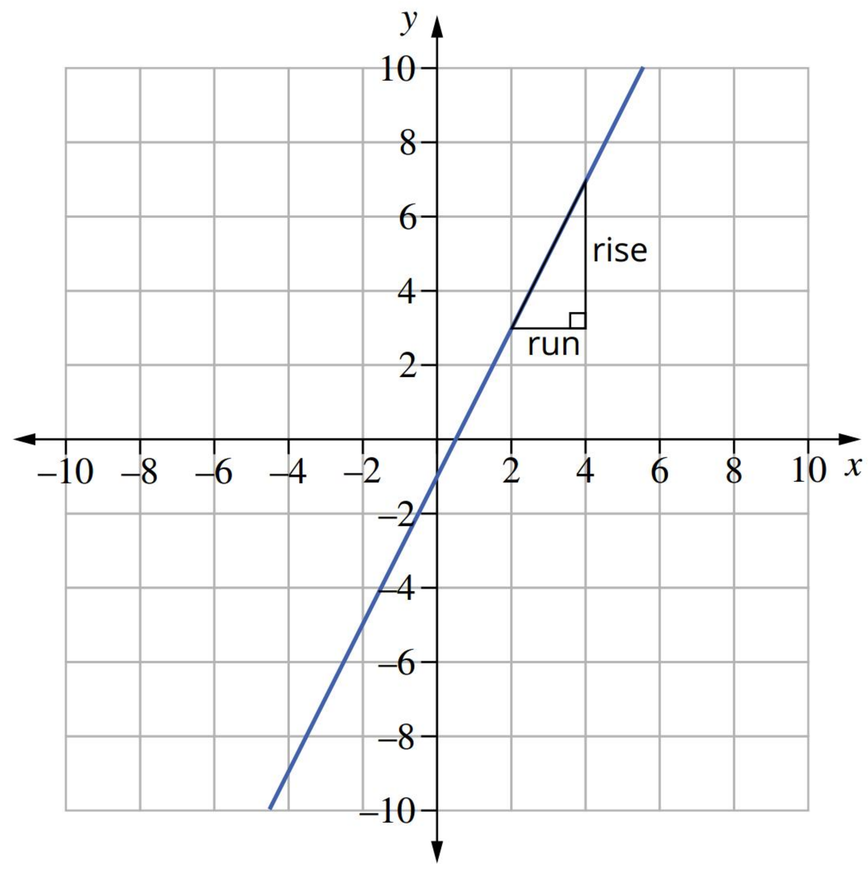


FIGURE 1.3.1 A graph representing a simple relationship between two variables

The y-intercept and gradient can be easily calculated by hand or with technology. The gradient of any straight line is calculated using:

$$\text{gradient, } m = \frac{\text{rise}}{\text{run}} = \frac{\Delta y}{\Delta x}$$

The y-intercept, c, is read off the y-axis.

The equation of any straight line is determined by the gradient and y-intercept:

$$y = mx + c$$

In the graph shown in Figure 1.3.1, the equation of the straight line is $y = 2x - 1$, with a gradient of 2 and y-intercept of -1.

SKILLBUILDER 1.3.1

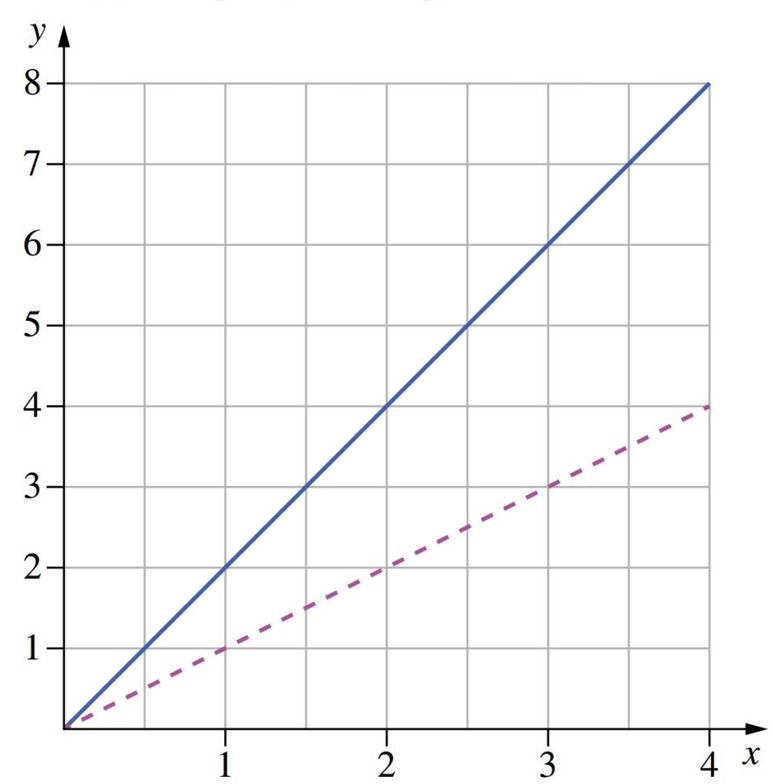
Interpreting the slope of a linear graph

Scientists often represent a relationship between two variables as a graph. For directly proportional relationships, the variables are related to each other by a straight line, where the slope (or gradient) of the line represents the constant of proportionality between the two variables.

The slope or gradient of the line is defined as the ratio of change between two points in the vertical axis (Δy), divided by the change between two points in the horizontal axis (Δx). In other words, it measures the rate at which one variable (the dependent variable) changes with respect to the other (the independent variable).

The slope of a linear graph indicates the rate of change of the dependent variable (y-axis) with respect to the independent variable (x-axis). The graph on the right has two straight lines with different slopes.

The steeper slope (solid line) indicates that the rate of change is higher. This means the change is happening more quickly. On the other hand, the flatter slope (dashed line) indicates that the rate of change is lower. This means the change is happening more slowly.



Worked example 1.3.2

INTERPRETING THE SLOPE OF A LINEAR GRAPH

On a graph with two sloped lines, identify what the steeper sloped line indicates.

A a faster rate of change
B a slower rate of change
C the same rate of change
D a much slower rate of change

Thinking	Working
The slope or gradient of the line is defined as the ratio of change between two points in the vertical axis (Δy), divided by the change between two points in the horizontal axis (Δx).	A is correct. The steepness of the slope indicates the rate of change. A line with a steeper slope indicates a faster rate of change.

➤ Try yourself 1.3.2

INTERPRETING THE SLOPE OF A LINEAR GRAPH

Identify which of the following options indicates the rate of change of a straight line on a graph.

A area under the graph
B *y*-intercept
C *x*-intercept
D gradient

1.3 Review

SUMMARY

- When conducting mathematical operations or calculations, remember that all the rules of mathematics apply, including:
  - order of operations
  - rules for transposing formulas and working with fractions
  - substitutions
  - approximations.

KEY QUESTIONS

Describe

1 State the formula for calculating the gradient of a straight line.

Apply

2 Determine these quantities.

a the mass of 75 mL of ethanol (density of ethanol is 0.789 g mL^{-1})

b the volume of 24.5 g of ethanol

Analyse

3 A student recorded the following temperatures of water.

Time (min)	Temperature (°C)
0	22
2	34
4	43
5	50
8	64
10	78

a Calculate the average temperature change per minute during the experiment.

b Determine whether the increase was constant throughout the experiment.

1.4 Units

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- appreciate that chemistry uses the International System of Units (SI)
- recall fundamental units, their symbols and definitions
- convert between various units of the same type using SI and some non-SI units.

Science uses a specific system of units to describe measurements that are made. In chemistry, measurements are made using the International System of Units (SI). Most countries around the world use and understand these units as they are internationally accepted in science, commerce, sport and everyday life.

MEASUREMENT AND UNITS

Scientists use conventional ways of writing numerical measurements, such as SI units. Make sure the units you measure or observe are accurate and remember to use SI units when recording your evidence. Table 1.4.1 presents common quantities and SI units used in chemistry.

TABLE 1.4.1 Common quantities and SI units used in chemistry

Quantity	Symbol for quantity	Unit
mass	*m*	gram (g) kilogram (kg)
volume	*V*	litre (L) millilitre (mL)
amount of substance	*n*	mole (mol)
molar mass	*M*	grams per mole ($g\,mol^{-1}$)
relative molecular or formula mass	M_r	no units; relative to one atom of ^{12}C exactly
relative atomic mass	A_r	no units; relative to one atom of ^{12}C exactly
energy	*E*	joule (J) kilojoule (kJ)
concentration (molarity)	*c*	moles per litre ($mol\,L^{-1}$, M or $mol\,dm^{-3}$)
density	*d*	$g\,mL^{-1}$ or $kg\,L^{-1}$
temperature	*T*	°C, K
pressure	*P*	Pa

Correct use of unit symbols

The correct use of unit symbols removes ambiguity, as symbols are recognised internationally. Some important points to keep in mind when writing units and recording measurements and numbers are given in Table 1.4.2.

Upper case letters are only used for the *symbols* of the units that are named after people. For example, the unit of energy is joule and the *symbol* is J. The joule was named after James Joule, who was famous for studies on energy conversions. The exception to this rule is 'L' for litre. Upper case 'L' is used because a lower case 'l' looks like the numeral '1'.

The product of a number of units is shown by separating the symbol for each unit with a space. The division or ratio of two or more units can be shown in fraction form, using a slash, or using negative exponents. Prefixes should not be separated by a space.

TABLE 1.4.2 Examples of correct and incorrect use of symbols for derived units

Rule	✓	✗
Numbers and symbols should not be mixed with words.	Thirty grams 30 g	thirty g 30 grams
Do not put spaces between prefixes and unit symbols.	kg mL kPa	k g m L k Pa
Write the correct case for symbols (upper or lower case).	1 mm 84 kg 5.2 mL	1 Mm 84 KG 5.2 ml
SI units should not be followed by a full stop unless they are at the end of a sentence. The symbols for units are not abbreviations.	12.1 mm	12.1 mm.
Only use upper case letters for unit symbols named after people. The exception is 'L' for litre, to avoid confusion because 'l' looks like the numeral '1'.	J (the unit of energy is joule, named after James Joule)	j
Units can take the plural form by adding an 's' when used with numbers greater than one. Never do this with the unit symbols.	Two kilojoules 2 kJ	2 kJs
The product of two or more units is shown by separating the symbol for each unit with a space.	0.1 mol dm^{-3}	0.1 mol dm^{-3}
The division or ratio of two or more units can be shown in fraction form, using a slash, or using negative exponents.	0.1 mol dm^{-3} 0.1 mol/dm^3	0.1 mol/dm^{-3}
When units are displayed with a negative exponent such as g mL^{-1}, the negative value of the exponent signifies the division of the units, or per unit. In this case, g mL^{-1} is the same as g/mL, or grams per millilitre.	1000 kJ mol^{-1} 13°C/g	1000 kJ/mol^{-1} 13°C/g^{-1}

When units are displayed with a negative exponent, such as mol L^{-1}, the negative value of the exponent signifies the division of the units; in other words, per unit. In this case, mol L^{-1} is the same as mol/L, or moles per litre.

Worked example 1.4.1

CALCULATIONS WITH UNIT CONVERSIONS

Calculate how many litres are in one cubic kilometre.

Thinking	Working
Write each volume in terms of m^3. (Remember that a km^3 is a cube that has sides of 1000 m by 1000 m by 1000 m.)	1000 L = 1 m^3 so 1 L = 0.001 m^3 1 km^3 = 1000 m × 1000 m × 1000 m = 10^9 m^3
Divide the volumes.	number of litres = $\frac{10^9}{0.001} = 10^{12}$
Check that your answer makes sense.	A litre is much smaller than a cubic kilometre, so the answer should be very large.
State the answer.	There are 10^{12} or one trillion litres in one cubic kilometre.

➤ Try yourself 1.4.1

CALCULATIONS WITH UNIT CONVERSIONS

If a person weighs 6.0×10^1 kg and the mass of a single carbon atom is 1.99×10^{-23} g, calculate how many carbon atoms would be needed to equal the mass of the person.

1.4 Review

SUMMARY

- Scientists use conventional ways of writing numerical measurements such as using the International System of Units (SI).
- Units with a prefix need to be converted into scientific notation before they can be used in a chemistry formula.
- When units are displayed with a negative exponent, the negative value of the exponent signifies the division of the units. For example, $g\,mL^{-1}$ is the same as g/mL, or grams per millilitre.
- When writing and recording measurements, remember:
  - do not mix numbers and symbols with words
  - do not put spaces between prefixes and unit symbols
  - use the correct case for symbols (upper or lower case).

KEY QUESTIONS

Describe

1 State the standard unit of measurement, and the symbol, for the following quantities.

a time
b temperature
c length
d mass

2 List the following prefixes from largest to smallest: centi, milli, deci, mega, kilo, nano, micro.

Apply

3 Explain why it is important that general society, not just the scientific community, has a systematic and consistent set of units for measurement.

Analyse

4 Convert 30.00 mL into L.

5 Identify any errors in the measurements below and correct them.

a $23\,mL/g\,h^{-1}$
b $79\,kl\,s^{-1}$
c four litres
d 1.56 grams

6 Determine how many metres there are in the 656 nm wavelength of red light emitted from hydrogen.

7 Determine how many atoms there are in 5.3 g of helium.

1.5 Measuring precision and accuracy using uncertainty and percentage error

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- explain the difference between accuracy and precision
- explain the difference between uncertainty and error
- calculate uncertainty and error values for measurements
- write measurements with uncertainty and error values
- write measurements and calculations to the correct number of significant figures
- perform calculations that contain uncertainty or error values
- understand that all measurements made in chemistry experiments are subject to a level of uncertainty
- differentiate between accuracy and precision, and know how to express these quantitatively using significant figures
- perform calculations using significant figures
- explain the difference between mistakes, systematic uncertainties and random uncertainties
- determine the absolute measurement uncertainty of a value based on the precision of the instrument
- determine the uncertainty of a mean using the range of trials
- convert between absolute and percentage uncertainties
- calculate a value along with the associated uncertainty.

All measurements are limited by the instrument used and the observer. Accuracy of the measurements and results are therefore affected. Instruments have a prescribed level of precision and cannot measure within the smallest increment of the device. In addition, a scientist's technique and experience with the instrument influences the precision with which the reading can be made.

However, in science, it is impossible to measure the true value, as there will always be some degree of **uncertainty**. This results in **error** and uncertainty in the values measured or observed. Therefore, science can be thought of as developing evidence-based results that have some limitations. Measurements with uncertainty and errors are normal in science, so results are always presented with a **range** (e.g. ±0.5), indicating possible precision, or processed through statistical calculations.

ACCURACY AND PRECISION

In science and statistics, the terms 'accuracy' and 'precision' have very specific and different meanings.

- **Accuracy** is the ability to obtain the correct measurement. To obtain accurate results, you must minimise **systematic errors**.
- **Precision** is the ability to consistently obtain the same measurement. To obtain precise results, you must minimise **random errors**.

To understand more clearly the difference between accuracy and precision, think about aiming at the bullseye on a target (Figure 1.5.1). Accuracy is being able to hit the bullseye, whereas precision is being able to hit the same spot every time. In summary, measurements should be both as precise and accurate as possible.

Any measurement made in chemistry needs to be both accurate and precise.

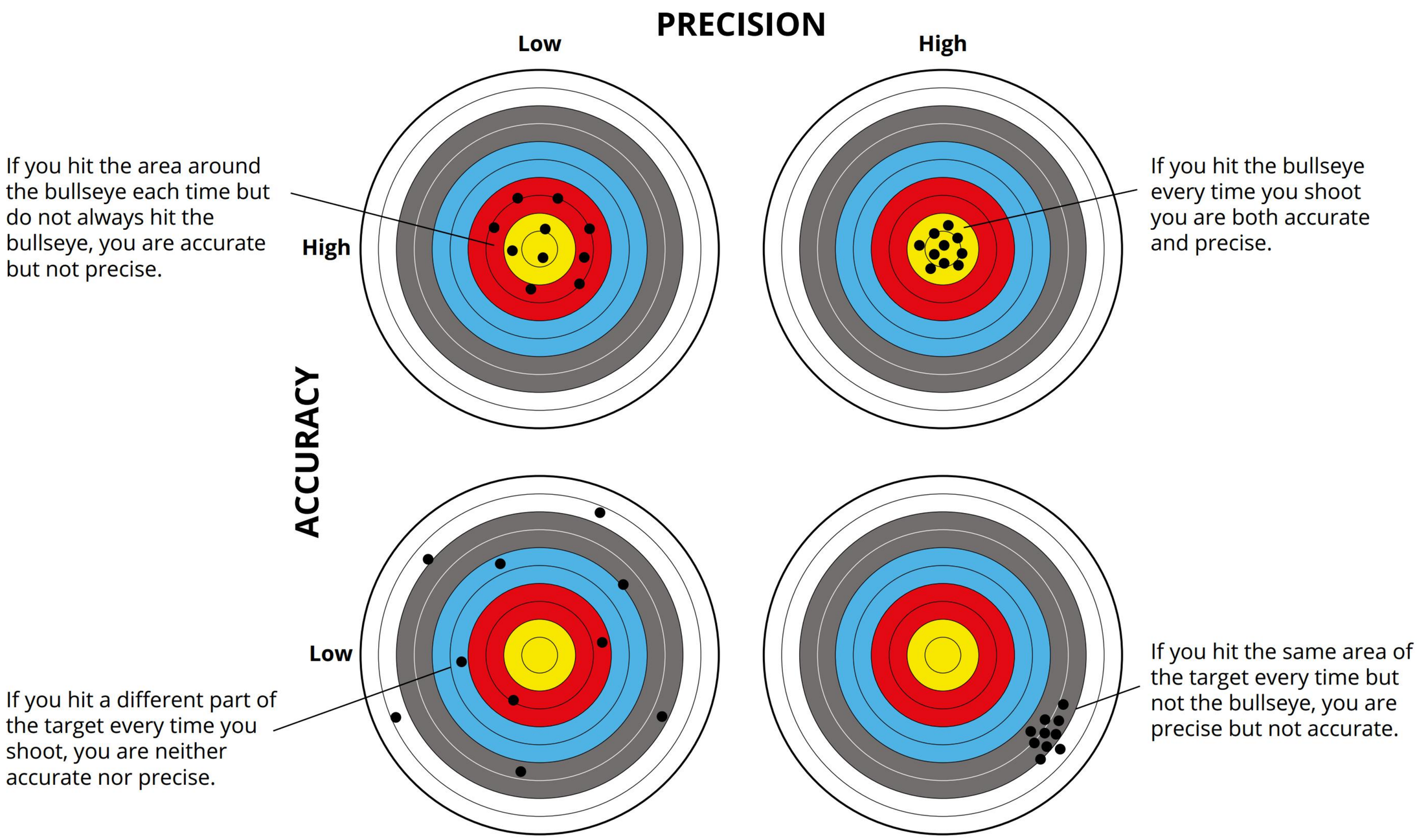


FIGURE 1.5.1 An example of a target illustrates the difference between accuracy and precision.

Recording numerical data

When using instruments to measure data, the number of significant figures (or digits) and decimal places you use is determined by how precise your measurements are.

The overall precision of the measurement depends on the scale, accuracy and precision of the instrument and the technique you are using (Figure 1.5.2). For example, a beaker may be used to measure volumes approximately and has limited accuracy of, for example, ±5%; however, a graduated pipette is much more accurate, with accuracies of ±0.1% or ±0.2%. In addition, your pipette may be accurate but if your technique using the pipette is variable, the overall accuracy and precision will be limited.

When you record **raw data** and report **processed data**, you must use the number of significant figures available from your equipment or **observation**. (This is discussed in more detail in Module 1.11.) Using either a greater or smaller number of significant figures can be misleading. For example, Table 1.5.1 shows measurements of five mass samples taken using an electronic balance accurate to 2 decimal places. The data was entered into a spreadsheet to calculate the mean, which was displayed with 4 decimal places. You would record the mean as 20.83 g, not 20.8260 g, because 2 decimal places is the precision limit of the instrument. Recording 20.8260 g would be an example of false precision.

TABLE 1.5.1 An example of false precision in a data calculation

Sample	1	2	3	4	5	Mean
Mass (g)	20.13	20.62	21.22	20.99	21.17	20.8260

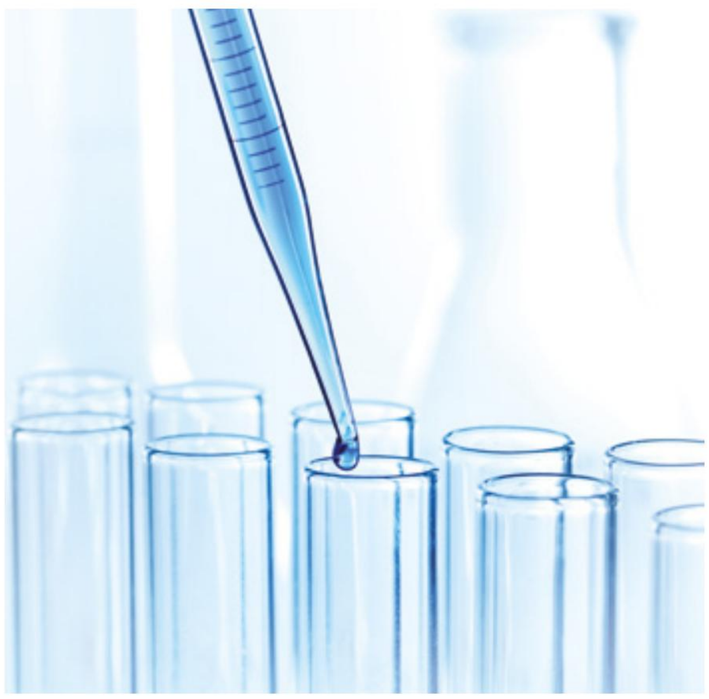


FIGURE 1.5.2 A 5 mL graduated pipette can measure volumes to an accuracy of one-tenth of a millilitre. The pipette has major divisions of 1 mL and minor divisions of 0.1 mL.

UNCERTAINTY AND ERROR

Uncertainty is a range of measurements from an experiment within which the true value is expected to lie. Due to variations, an estimation is made to suggest where the true value should be found among the measurements. Expressed as a ± value, uncertainty can be derived either from the known precision of the equipment or from calculations involving the range of trials.

Error is the difference between a measurement and the true value. This is not just an indication of human error or mistakes, but is mainly due to the unlikelihood of recording the true value in any given measurement. It is due to an inability to achieve the true value. Error cannot be eliminated, and therefore it is important to understand, record and report it. Two types of error can occur—systematic errors and random errors (Table 1.5.2).

TABLE 1.5.2 Systemic and random errors

Error	Definition	Cause	Example
systematic	An error in measurements caused by the design of a system (e.g. methodology) or instrument (uncalibrated), which results in the measurements shifting in a systematic direction. The mean may be displaced or varied in a predictable way affecting the accuracy of the measurement. It is quantified by calculating percentage error.	• instrument calibration • choice of instrument • precision of instrument (increments) • precision of instrument (sample rate, samples per second) • sampling (the choice of population or representatives) • heat loss to the surroundings	The balance used for weighing out samples reads 0.05 g too high for all your masses because it was improperly tared (set to zero) at the start of the experiment.
			Using a standard hydrochloric acid solution for a series of titrations that is not 1.0 M. As long as the actual concentration of the acidic solution is determined, the number of moles of base required to neutralise it in each titration can be corrected for.
random	An error that affects the measurement in an unpredictable way, resulting in an even variation (fluctuation) in measurements above and below the expected true value. This affects the precision of the measurement. It is quantified by calculating uncertainty.	• estimation (measuring between increments) • sampling (frequency, spread, increments) • parallax (incorrect angle for viewing instrument scale) • instrument sensitivity • noise (random irregularity)	Using a universal indicator to determine the pH of a solution, in which the pH must be estimated by the shade and colour of the paper (e.g. yellow/orange versus bright orange).
			Measuring the time taken for a reaction to occur has a random error associated with the identification of when the reaction is judged to be complete.

Uncertainties and errors should always be calculated or measured and then reported. They then form part of the analysis and interpretation (see Module 1.7).

Calculating uncertainty in measurement

The goal when taking measurements is to obtain repeat values (trials) that closely agree. We expect repeat measurements to vary somewhat based on the precision of the equipment. For example, when using a measuring cylinder for the volume of solution, the **measurement uncertainty** of an analogue instrument is half the smallest increment (for digital, it is the smallest decimal place on the readout). Using the particular instrument, the true value is expected to fall within this range (e.g. measured value ±0.15 mL for a 150 mL volumetric cylinder).

$$\text{measurement uncertainty} = \pm \frac{\text{smallest increment}}{2}$$

When averaging repeat measurements, the uncertainty should be reported alongside your average. Known as the **uncertainty of the mean,** it represents the precision of the method, expressed as the range of experimentally obtained values. The following equation is a simple way to calculate the uncertainty of the mean.

$$\text{uncertainty of the mean} = \pm \frac{\text{upper value} - \text{lowest value}}{2}$$

Worked example 1.5.1

CALCULATING UNCERTAINTY OF THE MEAN

A titration was performed three times and the volumes of acid required to neutralise the solution were 20.8, 21.4 and 20.2 mL. The average volume of acid used was 20.8 mL. Calculate the uncertainty of the mean, then write the average volume including the uncertainty.	
Thinking	**Working**
Write the formula.	$\text{uncertainty} = \pm\frac{\text{upper value} - \text{lowest value}}{2}$
Insert the values and then calculate.	$\text{uncertainty} = \pm\frac{(21.4 - 20.2)}{2}$ $= \pm\frac{1.2}{2}$ $= \pm 0.6\,\text{mL}$
Combine the measurement with the uncertainty.	20.8 mL ± 0.6 mL

➤ Try yourself 1.5.1

CALCULATING UNCERTAINTY OF THE MEAN

The rate of the reaction between sodium thiosulfate and sulfuric acid was measured by timing how long it took for the reaction mixture to turn opaque. The reaction was performed three times at each concentration of sulfuric acid and the average was calculated. For the 1.0 M solution, the time taken was 51, 47 and 58 s. The average time was 52 s. Calculate the uncertainty of the mean, then write the average time including the uncertainty.

In experimental investigations where a number of trials are performed, you have the opportunity to describe the level of uncertainty in two numerical ways, measurement uncertainty and uncertainty of the mean. When these uncertainties are expressed in the same units as the value they describe, they are an **absolute uncertainty** (e.g. 50 cm ± 0.5 cm).

SKILLBUILDER 1.5.1

Calculating absolute measurement uncertainty

Calculate the absolute measurement uncertainty for instrumental error during an experiment where the temperature was measured at 32°C using both a glass thermometer with increments of 1°C and a digital thermometer with increments of 0.1°C.

For the glass thermometer

1 Write down the formula.

$$\text{uncertainty} = \pm\frac{\text{smallest increment}}{2}$$

2 Insert the values and calculate.

$$\text{uncertainty} = \pm\frac{1}{2}$$
$$= \pm 0.5°\text{C}$$

3 Combine the measurement with the uncertainty.

32°C ± 0.5°C

For the digital thermometer

1 Write down the formula.

uncertainty = ± smallest increment

2 Insert the values and calculate.

uncertainty = ± 0.1°C

3 Combine the measurement with the uncertainty.

32.0°C ± 0.1°C

Uncertainty can also be reported as a percentage of the measurement; this is known as **percentage uncertainty**. To calculate the percentage uncertainty, apply this formula:

$$\text{percentage uncertainty (\%)} = \pm\left(\frac{\text{absolute uncertainty}}{\text{measurement}}\right) \times 100$$

Worked example 1.5.2

CALCULATING PERCENTAGE UNCERTAINTY FOR INSTRUMENTAL ERROR

The temperature during an experiment was measured and then reported at 32.00°C ± 0.05°C. Calculate the percentage measurement uncertainty. Write the temperature with the uncertainty.

Thinking	Working
Write the formula for percentage uncertainty.	percentage uncertainty $= \pm\left(\frac{\text{absolute uncertainty}}{\text{measurement}}\right) \times 100$
Insert the values and then calculate.	percentage uncertainty $= \pm\left(\frac{0.05}{32.00}\right) \times 100$ $= \pm 0.16\%$
Combine the measurement with the percentage uncertainty and express to the appropriate number of significant figures.	32.00°C ± 0.16%

➤ Try yourself 1.5.2

CALCULATING PERCENTAGE UNCERTAINTY FOR INSTRUMENTAL ERROR

The pH of a solution was determined to be 11.4 ± 0.6. Calculate the percentage measurement uncertainty. Write the pH with the uncertainty.

Calculating percentage error in values

As stated above, scientists try to calculate the 'true' or 'correct' value. However, due to equipment and/or method, experimental results may give an inaccurate value. The percentage error between the measured value and the true value provides information about the validity and systematic error, and can be calculated using the percentage error formula:

$$\text{percentage error (\%)} = \left|\frac{\text{measured value} - \text{true value}}{\text{true value}}\right| \times \frac{100}{1}$$

This formula can also be used to calculate the difference between the true value and the generally accepted value of a quantity, such as the density of water. The density of water is generally stated to be $1\,\text{kg}\,\text{m}^{-3}$; however, the exact density at 4.0°C is $0.999\,839\,5\,\text{kg}\,\text{m}^{-3}$. This calculation is shown in Worked example 1.5.3.

In this case, the measured value is replaced with the accepted value. The percentage error in the accepted (rounded) value of $1\,\text{kg}\,\text{m}^{-3}$ is less than 0.02%. This indicates that using $1\,\text{kg}\,\text{m}^{-3}$ is acceptable since the percentage error is very small and likely to be much smaller than experimental uncertainty.

Worked example 1.5.3

CALCULATING PERCENTAGE ERROR

Calculate the percentage error between the true density of water at 4.0°C ($0.9998395\,kg\,m^{-3}$) and the generally accepted (rounded) value of $1\,kg\,m^{-3}$.	
Thinking	**Working**
Write the formula.	$\text{percentage error (\%)} = \left\lvert \frac{\text{measured value} - \text{true value}}{\text{true value}} \right\rvert \times \frac{100}{1}$
Insert the values and then calculate.	$\text{percentage error (\%)} = \left\lvert \frac{1 - 0.9998395}{0.9998395} \right\rvert \times \frac{100}{1}$ $= \frac{0.0001605}{0.9998395} \times \frac{100}{1}$ $= 0.01605\%$

➤ Try yourself 1.5.3

CALCULATING PERCENTAGE ERROR

The laboratory technician made up a standard solution of 0.200 M. A student calculated the concentration of the solution to be 0.185 M. Calculate the percentage error.

Significant figures

When measuring phenomena during experimentation, the precision of the instruments determines the number of significant figures and decimal places you record in the data.

Significant figures convey meaning and precision, and the number of significant figures used depends on the scale of the instrument. You should record data using the number of significant figures available from the equipment or observation. Using either a greater or smaller number of significant figures is misleading.

When writing an answer to the correct number of significant figures, you may need to use rounding if the initial answer has more figures (digits) than you need. These extra figures are called 'non-significant figures'. If the first non-significant figure is ≥5, round up the number. If the first non-significant figure is <5, then do not round up. For example, if the initial answer for a calculation was 2.1259, but you only needed an answer to 3 significant figures, you would round it to 2.13. If the initial answer was 2.1241, this becomes 2.12, rounded to 3 significant figures.

SKILLBUILDER 1.5.2

Identifying significant figures

When giving an answer to a calculation, it is important to take note of the number of significant figures that you use.

You should give an answer that is as accurate as possible. However, an answer cannot be more precise than the data or the measuring device used to calculate it. For example, if an electronic balance that measures to the nearest gram shows that an object has a mass of 56 g, then the mass should be recorded as 56 g, not 56.0 g. This is because you do not know whether it is 56.0 g or 56.1 g or 56.2 g or 55.8 g.

The number 56 has 2 significant figures. Recording to 3 significant figures (e.g. 56.0 g or 55.8 g) would not be scientifically 'honest'.

If this mass of 56 g is used to calculate another value, it would also not be 'honest' to give an answer that has more than 2 significant figures.

Determining the number of significant figures to give in an answer depends on the kind of calculation you are doing.

- If you are multiplying or dividing, use the smallest number of significant figures provided in the initial values.
- If you are adding or subtracting, use the smallest number of decimal places provided in the initial values.

Working out the number of significant figures

Use the following rules to avoid confusion in determining how many significant figures are in a number.

1. All non-zero digits are always significant; for example, 21.7 has 3 significant figures.
2. All zeros between two non-zero digits are significant; for example, 3015 has 4 significant figures.
3. A zero to the right of a decimal point and following a non-zero digit is significant; for example, 0.5700 has 4 significant figures.
4. Any other zero is not significant, as it will be used only for locating decimal places; for example, 0.005 has just 1 significant figure.

Worked example 1.5.4

IDENTIFYING SIGNIFICANT FIGURES

a Identify which of the following is written to 2 significant figures.

A 30.1
B 0.00040
C 0.5
D 5.12

Thinking	Working
The zeros that come before the non-zero digit 4 are not significant, whereas those that follow 4 are significant.	B is correct. A has 3 significant figures. C has 1 significant figure. D has 3 significant figures.

b George multiplied 1.22 by 1.364. Identify which of the options below shows the result of this multiplication with the correct number of significant figures.

A 1.66
B 1.664
C 1.65
D 1.7

Thinking	Working
$1.22 \times 1.364 = 1.66408$	A is correct. When two numbers are multiplied, use the smallest number of significant figures in the initial values to report your answer. In George's multiplication, the answer is 1.66408, but since 1.22 has only 3 significant figures, the correct answer is 1.66.

➤ Try yourself 1.5.4

IDENTIFYING SIGNIFICANT FIGURES

Identify which of the following is written to 4 significant figures.

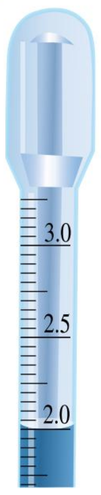
A 0.0041
B 0.410
C 41.00
D 4100

Worked example 1.5.5

ACCURATELY RECORDING MEASUREMENTS FROM INSTRUMENTS

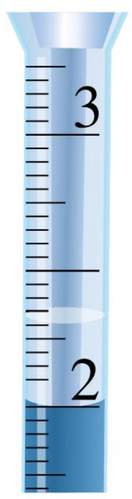
When measuring the amount of solution for an acid–base experiment, you need to record the results accurately and be able to identify the appropriate number of significant figures to use. The numbered markings on the pipettes below are in mL.

a State the measurement for the liquid level shown on this plastic pipette and identify the number of significant figures in this result.



Thinking	Working
The increments shown on the plastic pipette determine the accuracy with which the measurement can be recorded. If you record the measurement to more or fewer numbers, it becomes inaccurate.	The plastic pipette is marked with increments of 0.05 mL; therefore, all results must be recorded to the nearest 0.05 mL, with 2 decimal places.
Determine where the meniscus (the lowest point) of the liquid falls.	The meniscus of the liquid in the pipette is closest to the 2.00 mL marking; therefore, the result must be recorded as 2.00 mL, not as 2.0 mL.
Determine the number of significant figures included in this measurement.	The measurement of 2.00 mL has 3 significant figures.

b State the measurement for the liquid level shown on this glass pipette and identify the number of significant figures in this result.



Thinking	Working
The increments shown on the glass pipette determine the accuracy with which the measurement can be recorded. If you add extra numbers or remove numbers, it becomes inaccurate.	The glass pipette is marked with increments of 0.05 mL; therefore, all results must be recorded to the nearest 0.05 mL, with 2 decimal places.
Determine where the meniscus (the lowest point) of the liquid falls.	The meniscus of the liquid in the pipette is closest to the 2.00 mL marking; therefore, the result must be recorded as 2.00 mL, not as 2 mL.
Determine the number of significant figures included in this measurement.	The measurement of 2.00 mL has 3 significant figures.

➤ Try yourself 1.5.5

ACCURATELY RECORDING MEASUREMENTS FROM INSTRUMENTS

When measuring the temperature for a calorimeter experiment, you need to record the results accurately and be able to identify the appropriate number of significant figures to use.

a State the measurement shown on this glass alcohol thermometer, and identify the number of significant figures in this result.

b State the measurement shown on this digital thermometer, and identify the number of significant figures in this result.

Significant figures are the exact digits observed when recording the results of an observation or experiment. For example, if the volume of O_2 gas produced and measured from the electrolysis of water in a 20-minute experiment was 6.0 mL because exactly 6.0 mL was observed, then the measurement is 6.0 mL with 2 significant figures, not 6 mL.

Table 1.5.3 shows some examples of measurements and how many significant figures they have.

TABLE 1.5.3 Measurements and significant figures

Measurement	Number of significant figures
15	2
3.5	2
3.50	3
0.037	2
1401	4
1400	2

It is important to record the exact numbers measured during an experiment. This determines the significant figures, and later the accuracy and precision of the analysis. If a zero is observed, record it, as it is the exact amount measured. This includes all zeros before and after decimal places.

Using either a greater or smaller number of significant figures can be misleading. For example, Table 1.5.4 shows three measurements to 2 decimal places (4 significant figures). The data were entered into a spreadsheet to calculate the mean, which was displayed with 3 decimal places. You would record the mean as 19.52 mL, not 19.517 mL, because 2 decimal places is the precision limit of the instrument. Recording 19.517 g would be an example of false precision.

TABLE 1.5.4 An example of false precision in a data calculation

Trial	1	2	3	Mean
Volume (mL)	19.45	19.55	19.55	19.517

Determining uncertainty in a single measurement

When using an instrument to measure a property of an object, there will always be a limit as to how precise the reading can be.

The precision that can be read off a single instrument is called the limit of reading. This is the smallest visible increment on an analog instrument, or if a digital instrument is used, then the limit of reading is usually the smallest decimal place given on the screen.

For most analog instruments, the absolute uncertainty, Δx, in a measurement of x is exactly half of the limit of reading for each part of the measured object that has to be lined up. This means that the actual measurement could be anywhere from *half* of the smallest increment too big to *half* of the smallest increment too small.

Some analog instruments have a zero mark and a reading mark, such as the ruler shown in Figure 1.5.3a. The object to be measured has to be lined up at *both* ends, thus doubling the absolute uncertainty. For instance, when using rulers or burettes, the absolute uncertainty is equal to the limit of reading, rather than half of it.

In a digital instrument, Δx is typically the limit of reading, or the smallest decimal place given on the screen. An example of this is a high-precision electronic balance shown in Figure 1.5.3b.

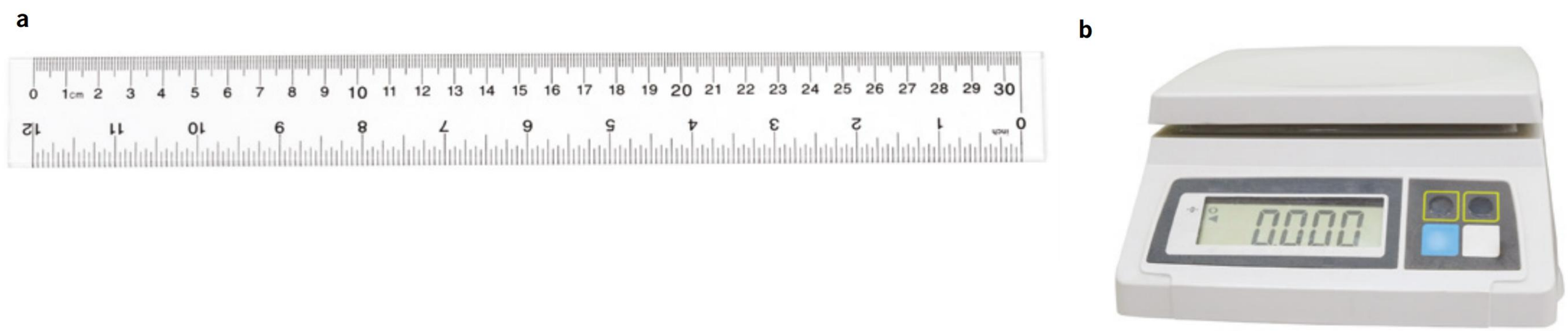


FIGURE 1.5.3 (a) A ruler with a limit of reading of 1 mm. (b) An electronic balance with a limit of reading of 0.001 g.

Usually, the absolute measurement uncertainty in a measurement will have one significant figure, or two significant figures if the first digit is 1. This is done because the uncertainty of a measurement is meant to be an estimate and writing more than two significant figures is therefore unhelpful.

For analog instruments that have one scale to line up (such as a measuring cylinder, thermometer or voltmeter), the absolute measurement uncertainty is half of the smallest increment scale, or limit of reading.

For analog instruments that have two scales to line up (such as rulers and burettes), the absolute measurement uncertainty is equal to the smallest increment scale, or limit of reading.

For digital instruments, the absolute measurement uncertainty is equal to the smallest decimal place displayed.

When the absolute uncertainty has been determined, the measurement should be rounded so that it and the absolute uncertainty have the same number of *decimal places*. This is to keep the measurement and its uncertainty to the same precision. Examples of measurements and their absolute uncertainties are shown in Table 1.5.5.

TABLE 1.5.5 Examples of writing a measurement and its absolute uncertainty

Measurement and absolute uncertainty	Comments
48.2 ± 1.0°C	The absolute uncertainty is written to 2 significant figures because the first digit is 1. The measurement and uncertainty then have the same number of decimal places.
99.99 ± 0.01 s	The measurement and absolute uncertainty are written to 2 decimal places, with one significant figure for the uncertainty. This measurement of time may have been recorded using a digital device, such as a data logger, since the precision is quite high.
0.000 000 031 ± 0.000 000 005 kg	This is technically a correct way of writing a measurement and its absolute uncertainty, but it is normally written in scientific notation so that the measurement and uncertainty have the same power of 10, i.e. $(3.1 \pm 0.5) \times 10^{-8}$ kg.

The limit of reading and absolute uncertainties of common equipment used in a chemistry laboratory are shown in Table 1.5.6.

TABLE 1.5.6 A summary of common instruments and their uncertainties

Instrument	Type of instrument	Limit of reading	Absolute uncertainty	Example	Notes
mm ruler	analog	1 mm	± 1.0 mm	123.8 ± 1.0 mm	Half of the limit of reading is 0.50 mm, but since the object to be measured has to be lined up at both ends, the uncertainty is double this, or ±1.0 mm.
cm ruler	analog	1 cm	± 1.0 cm	31.4 ± 1.0 cm	Half of the limit of reading is 0.50 cm, but since the object to be measured has to be lined up at both ends, the uncertainty is double this, or ±1.0 cm.
thermometer	analog	1.0°C	± 0.5°C	24.4 ± 0.5°C	Only the top part of the liquid in the thermometer has an uncertainty, so the uncertainty is exactly half of the limit of reading.
measuring cylinder	analog	1.0 mL	± 0.5 mL	15.7 ± 0.5 mL	The limit of reading and absolute uncertainty depend on the size of the measuring cylinder.
burette	analog	0.1 mL	± 0.1 mL	20.10 ± 0.1 mL	Half of the limit of reading is 0.05 mL, but since the object to be measured has to be lined up at both ends, the uncertainty is double this, or ±0.1 mL.
volumetric pipette	analog	varies	varies, ± 0.03 mL	25.00 ± 0.03 mL	The uncertainty for the pipette is based on the precision given on the pipette. The precision varies based on the size and quality of the pipette.
stopwatch	digital	0.01 s	from ± 0.1 s to ± 0.4 s	9.6 ± 0.2 s	The limit of reading is not the absolute uncertainty for a stopwatch because the user's reaction time (usually between 0.1 and 0.4 s) needs to be taken into consideration.
electronic balance	digital	typically 0.01 g	± 0.01 g	7.03 ± 0.01 g	The limit of reading is usually the smallest decimal place given on the screen.

These steps will help you write a measurement and its absolute uncertainty.

1 Determine the absolute uncertainty from the type of instrument used to measure the quantity.
2 Measure the quantity, including an estimate of the final significant figure.
3 If the first digit of the absolute uncertainty is 1, then one more significant figure can be quoted. Usually, this extra digit is zero.
4 The measurement is then rounded up or down to the same number of decimal places, or place value holders, as the uncertainty; however, the uncertainty should not be presented to more than 2 significant figures.
5 Do not forget the unit of measurement for the quantity.

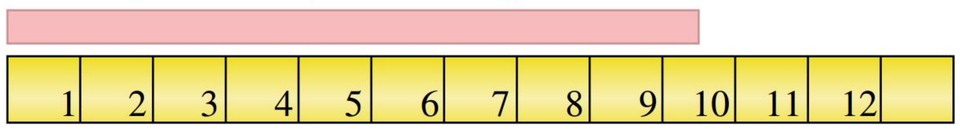
The absolute uncertainty should be written to 1 or a maximum of 2 significant figures.

Worked example 1.5.6

READING MEASUREMENTS

For each of the following objects, determine its measurement and uncertainty.

a the length of the pink rectangle measured with a ruler calibrated in centimetres



Thinking	Working
The pink rectangle is between 9 cm and 10 cm in length, so the best estimate for this is 9.5 cm.	length, $L = 9.5$ cm
The limit of reading is 1.0 cm, so this is the uncertainty in this centimetre ruler.	$\Delta L = \pm 1.0$ cm
Write the measurement and uncertainty.	$L = 9.5 \pm 1.0$ cm

b the temperature of tap water measured using an analog thermometer

Thinking	Working
The temperature is between 20°C and 21°C, with the best estimate of 20.2°C.	temperature, $T = 20.2$°C
The limit of reading is 1.0°C, so the uncertainty is half of this, i.e. 0.5°C.	$\Delta T = \pm 0.5$°C
Write the measurement and uncertainty.	$T = 20.2 \pm 0.5$°C

c the temperature of tap water measured using a digital thermometer

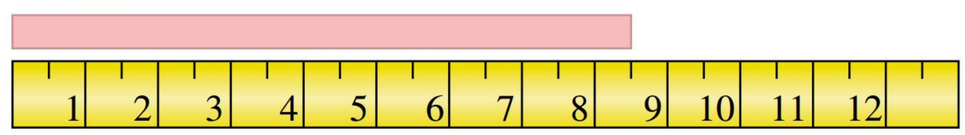
Thinking	Working
This temperature measurement is made using a digital thermometer, so the temperature is simply read off the screen as 31.2°C.	temperature, $T = 31.2°C$
The uncertainty in this measurement is equal to the smallest decimal value displayed, i.e. ± 0.1°C.	$\Delta T = \pm 0.1°C$
Write the measurement and uncertainty.	$T = 31.2°C \pm 0.1°C$

➤ Try yourself 1.5.6

READING MEASUREMENTS

For each of the following objects, determine its measurement and uncertainty.

a the length of the pink rectangle measured with a ruler with increments of 0.5 cm



b a red liquid in an analog measuring cylinder

c the mass of this donut measured on an electronic balance

Worked example 1.5.7

CALCULATING THE TOTAL UNCERTAINTY

Determine the uncertainty in the number of moles of NaOH in a 25 mL 1.00 ± 0.05 M NaOH solution measured out using a 25.00 ± 0.05 mL pipette.	
Thinking	**Working**
Write the formula.	number of moles = volume × concentration
Recall how to propagate the uncertainty.	Since the number of moles is calculated by multiplying the volume by the concentration, the total uncertainty is determined by the sum (addition) of the percentage uncertainties for each quantity.
Calculate the percentage uncertainties for each measurement.	percentage uncertainty of concentration $= \frac{\text{absolute uncertainty}}{\text{measurement}} \times \frac{100}{1}$ $= \frac{0.05}{1.00} \times \frac{100}{1}$ $= 5\%$ percentage uncertainty of volume $= \frac{\text{absolute uncertainty}}{\text{measurement}} \times \frac{100}{1}$ $= \frac{0.05}{25.00} \times \frac{100}{1}$ $= 0.2\%$
Calculate the number of moles (including the sum of the percentage uncertainties).	number of moles = volume × concentration $= 25.00 \times 1.00$ $= 25.0\text{ mL} \pm 5.2\%$

➤ Try yourself 1.5.7

CALCULATING THE TOTAL UNCERTAINTY

Calculate the density (including uncertainty) of a 10 ± 0.1 cm^3 block of wood weighing 24.3 ± 0.1 g.

Calculations with uncertainties

There are a few rules when conducting calculations with numbers (or measurements) that have uncertainties. It is important to record the correct uncertainty once all the calculations are done so that the appropriate accuracy is reported. Table 1.5.7 outlines the rules for undertaking calculations with data and its associated uncertainty.

Keep in mind that the rules for significant figures apply to all numerical reporting, including the uncertainties.

TABLE 1.5.7 Rules for calculations involving uncertainty

Calculation	Rule	Examples
addition and subtraction	add the absolute uncertainties	5.4 ± 0.05 + 3.2 ± 0.05 = 8.6 ± 0.10 5.4 ± 0.05 + 3.2 ± 0.10 = 8.6 ± 0.15 5.4 ± 0.05 – 3.2 ± 0.05 = 2.2 ± 0.10 5.4 ± 0.05 – 3.2 ± 0.10 = 2.2 ± 0.15
multiplication and division	add the percentage uncertainties	3.0 ± 0.05 × 1.5 ± 0.05 = 3.0 ± 1.7% × 1.5 ± 3.3% = 4.5 ± 5.0% 3.0 ± 0.05 ÷ 1.5 ± 0.05 = 3.0 ± 1.7% ÷ 1.5 ± 3.3% = 2.0 ± 5.0%
multiplying by a constant (absolute uncertainty)	multiply the uncertainty	3.14 × (4.10 ± 0.05) = 12.9 ± 0.16
multiplying by a constant (percentage uncertainty)	maintain the uncertainty	3.14 × (4.10 ± 1.6%) = 12.9 ± 1.6%

Worked example 1.5.8

PROPAGATING UNCERTAINTIES

A student uses a 20 mL pipette twice to measure out 40 mL of solution. If the uncertainty in the pipette is 0.05 mL, determine the uncertainty in the total volume measured.

Thinking	Working
Recall how to propagate the uncertainty.	Since the total volume is determined by the sum (addition) of the volumes, the uncertainties are also summed.
Write the formula.	total uncertainty = sum of uncertainty in each measurement Add the uncertainties: total uncertainty $= 0.05 + 0.05$ $= 0.10$
Write the volume and total uncertainty.	total volume = 40.00 ± 0.10 mL

➤ Try yourself 1.5.8

PROPAGATING UNCERTAINTIES

A student uses a 20 mL pipette four times to measure out 80 mL of solution. If the uncertainty in the pipette is 0.05 mL, determine the uncertainty in the total volume measured.

1.5 Review

SUMMARY

- Accuracy is the ability to obtain the correct measurement. To obtain accurate results, you must minimise systematic errors.
- Precision is the ability to consistently obtain the same measurement. To obtain precise results, you must minimise random errors.
- Uncertainty is a range of measurements from the experiment in which the true value is thought to lie. It is obtained using the precision of the measuring instrument (measurement uncertainty) or by calculations of repeat trials (uncertainty of the mean).
- Error is the difference between a measurement and the true value.
- Uncertainty values are presented as a range (e.g. ±0.3).
- A simple way to calculate the uncertainty of the mean is:

$$\text{uncertainty of the mean} = \pm\frac{(\text{upper value} - \text{lowest value})}{2}$$

- A simple way to calculate the measurement uncertainty is:

$$\text{measurement uncertainty} = \pm\frac{\text{smallest increment}}{2}$$

- The percentage uncertainty can be calculated using this formula:

$$\text{percentage uncertainty} = \pm\left(\frac{\text{absolute uncertainty}}{\text{measurement}}\right)\times 100$$

- The percentage error, when the experimental result can be compared with a theoretical or accepted result (value), can be calculated using this formula:

$$\text{percentage error (\%)} = \left|\frac{\text{measured value-true value}}{\text{true value}}\right|\times\frac{100}{1}$$

- The rules for calculations involving uncertainty are listed in the following table.

Calculation	Rule
addition and subtraction	add the absolute uncertainties
multiplication and division	add the percentage uncertainties
multiplying by a constant (absolute uncertainty)	multiply the uncertainty
multiplying by a constant (percentage uncertainty)	maintain the uncertainty

- Significant figures are a way of communicating how precise a measurement is.
- The number of significant figures used depends on the scale of the instrument.
- There are specific rules governing how many significant figures there can be in any measurement.
  - All non-zero digits are significant.
  - All zeros between non-zero digits are significant.
  - Trailing zeros (either decimal or not) if measured are significant.
  - Leading zeros are not significant (in numbers with decimals, they only inform where the decimal is placed).
- All measurements made in chemistry experiments are subject to a level of uncertainty or doubt as to the precision of that measurement.
- Accuracy is a description of how close a measurement is to the true value.
- Precision is a description of how many digits can be written down for a single measurement, or how close together a group of measurements are.
- Systematic errors arise due to mistakes in calibrating or using equipment the wrong way for every measurement.
- Random errors are naturally occurring and cannot be eliminated.
- The limit of reading of an instrument is the smallest increment on the instrument.
- Uncertainties are typically written as an absolute value or percentage.
- Measurement uncertainty represents the uncertainty in the readings due to limitations in equipment, reflecting the precision of the measurement. For example, if the best estimate of a volume is 5.0 cm^3 with a smallest increment of 0.2 cm^3, the measurement uncertainty is ±0.1 cm^3.
- Percentage error indicates the accuracy of the measured value by comparing the difference between the measured value and the true value. A lower percentage error signifies a more accurate measurement.
- Propagation of uncertainties involves the mathematical combination of uncertainties from a range of variables.

Continued over page

1.5 Review *continued*

- When adding or subtracting measurements, the individual absolute uncertainties always add.
- When multiplying or dividing measurements, the individual percentage uncertainties always add.
- When raising a measurement to a power, the percentage uncertainty is multiplied by the absolute value of the power.
- When using measurements in a formula, perform any addition and subtraction propagations first, followed by multiplication, division and exponents.

KEY QUESTIONS

Describe

1 Describe how values of uncertainty and error are presented.

2 State the absolute uncertainty of the following instruments.

a a ruler with 1 cm increments

b a protractor graduated in 1° intervals

c an electronic balance giving a reading to the nearest 0.001 g

d an analog needle voltmeter graduated in 10 V intervals

Apply

3 Explain the difference between accuracy and precision.

4 Explain why it would be unreasonable to state that the absolute uncertainty in a handheld digital stopwatch is ± the limit of reading or ±0.01 s.

Analyse

5 Calculate the average and the uncertainty of the mean for the two sets of data below.

Data set A: 11.4, 10.9, 11.8, 10.6, 11.5, 11.1

Data set B: 25.3, 27.4, 22.0, 26.1, 28.4, 23.1

6 Determine the absolute measurement uncertainty of the following instruments.

a a garden pH meter graduated in 0.2 intervals

b a burette graduated in 0.1 mL intervals

c an electronic balance giving a reading to the nearest 0.001 g

1.6 Tables and graphing

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- create tables to record and organise data
- present data from tables into graphs
- distinguish between types of graphs
- select appropriate graphs to represent data
- represent missing data in graphs
- explain what outliers are and know how to represent them in graphs.

PRESENTING DATA IN TABLES

Tables record number values and allow you to organise your data. In general, tables provide more detailed data than graphs, but it is easier to observe trends and patterns in data when they are in graph form than in table form.

Presenting raw data in tables

Tables organise data into rows and columns, and can vary in complexity according to the nature of your data. Tables can be used to organise raw data and processed data, or to summarise results.

The simplest form of a table is a two-column chart. The first column should contain the independent variable (the one you control) and the second column should contain the dependent variable (the one that may change in response to a change in the independent variable).

As you can see in Figure 1.6.1, tables should have the following features:

- a descriptive title
- column headings (including the units)
- aligned figures (align the decimal points)
- the independent variable placed in the left column.

Table 1. Volumes of NaOH needed to neutralise excess acid from the reaction of HCl with 1.2 g of calcium carbonate

	Volume of 0.5 M NaOH ± 0.5 (mL)			
Concentration of HCl (M)	**Trial 1**	**Trial 2**	**Trial 3**	**Average**
0.1				
0.3				
0.5				
0.7				
1.0				
2.0				

accurate descriptive title

independent variable in the left-hand column shows the units of measurement

dependent variable identifies the data set and shows the unit of measurement and the measurement uncertainty of the equipment

rows show the different concentrations of the solution used—the range of values for the independent variable

a minimum of five different data points for the independent variable

space for trials—in this case, three repeat trials were conducted

column to calculate the averages

FIGURE 1.6.1 Features of a good table

Presenting processed data in tables

Table 1.6.1 shows the relationship between temperature and average reaction rate. It displays reaction rate data in a processed format, because it displays the mean of several values for each temperature. To report processed data accurately, the uncertainty is also displayed; this will be a requirement for assessments.

TABLE 1.6.1 Effect of temperature on mean reaction rate, including uncertainty

Temperature (°C)	Average reaction rate (mol dm^{-3} s^{-1})
15	0.038 ± 0.002
25	0.043 ± 0.001
35	0.059 ± 0.001
45	0.074 ± 0.002

PRESENTING DATA IN GRAPHS

A **graph** is an incredibly useful tool. In chemistry, data is plotted using a line or curved graph, which is sometimes called a scatter plot.

Plotting data in graphs has many advantages.

- Data can be represented visually.
- Data points that are incorrect can be ignored.
- Constants can be determined from the properties of the line or curve.
- Uncertainties can be represented as **error bars**.
- A general **line of best fit** that matches the trend of the majority of the data points can be determined.
- Any known relationship between the dependent and independent variables can be supported or rejected, especially by the use of uncertainties.

Tables often provide more detailed data than graphs, but graphs can suggest a possible relationship between the dependent and independent variables, and highlight if no relationship exists. From the shape of the line or curve, it is easier to observe trends, patterns and gaps in data in graph form than in table form.

Graphs, like the one shown in Figure 1.6.2, are used when two variables are being considered and one variable is dependent on the other. The graph shows the relationship between the variables.

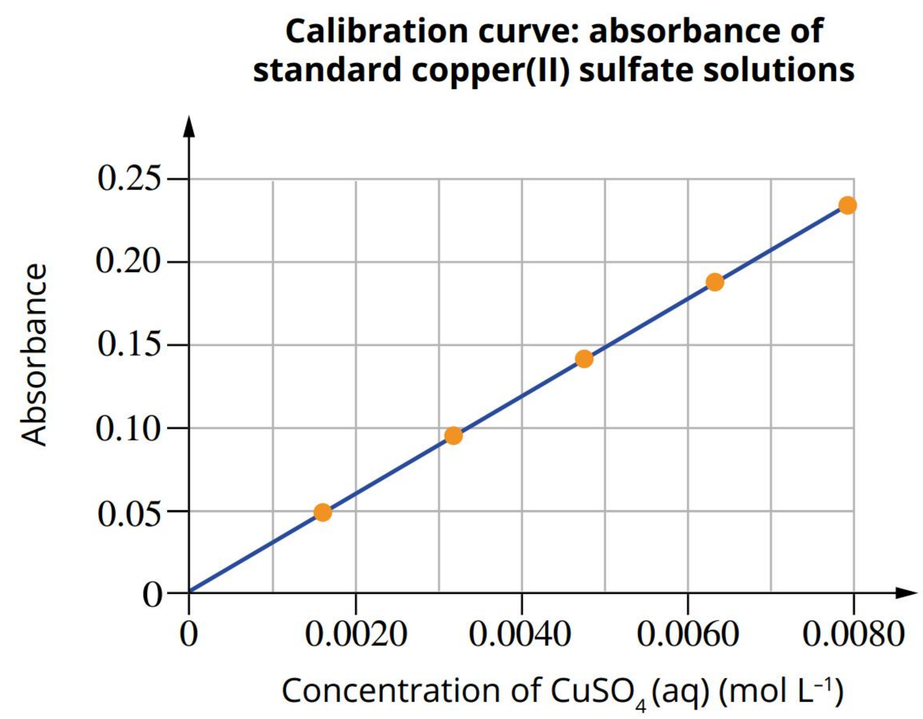


FIGURE 1.6.2 A graph showing the relationship between two variables: absorbance (dependent variable) and concentration of $CuSO_4$(aq) (independent variable)

DRAWING GRAPHS IN CHEMISTRY

For use in chemistry, every graph must have the following features.

1 The graph must have a suitable set of axes for the independent and dependent variables.

Most chemistry graphs are only drawn in the first quadrant, but some graphs use all four quadrants (i.e. have negative values for the independent and dependent variables).

Remember that:

- the independent variable is the variable that you deliberately change and always goes on the *x*-axis
- the dependent variable is the variable that changes in response to the independent variable and always goes on the *y*-axis.

2 The graph must have a suitable scale that allows information to be seen easily and quickly.

For most graphs, it is important to choose a scale that is linear and has tick marks at common intervals (e.g. 2, 5, 10, 100 units).

3 The title and axes must have labels. Make sure that the axis labels show information about the quantity and units. Give a descriptive title that is not just a repeat of the labels of the axes.

4 Data points should be plotted as a small circle or small cross indicating their position.

5 Error bars should be drawn for each point. These indicate the absolute uncertainties in the independent (a horizontal line) and dependent (a vertical line) values. They are drawn as a horizontal line centred on the data point indicating the independent variable's uncertainty left and right of the value, and as a vertical line centred on the data point indicating the dependent variable's uncertainty above and below the value. Combining the *x* and *y* error bars forms an error rectangle, within which true measurement is located (Figure 1.6.3).

The smaller the errors bars for a given point, the more precise the measurement is.

Graph showing an example of an error bar

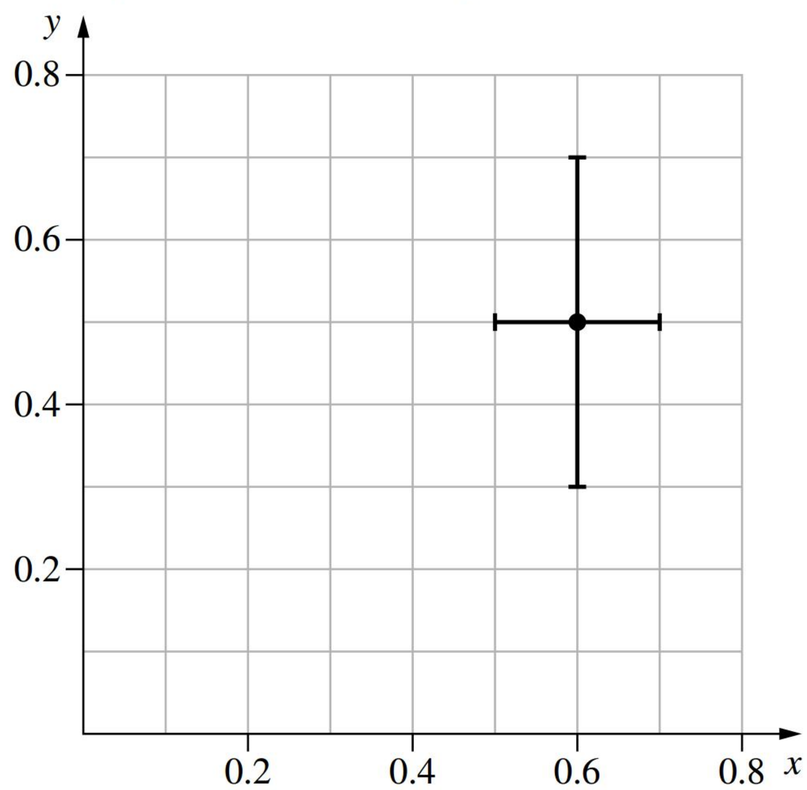


FIGURE 1.6.3 This error bar has an *x* value of 0.6 ± 0.1 and a *y* value of 0.5 ± 0.2.

Error bars are the graphical representation of the uncertainties in the independent and dependent variables.

The line of best fit

This is the straight line or a curve that best summarises the data. This line does not have to pass through every point or the origin, but does have to be one smooth continuous line or curve and *not* a 'join the dots' line (Figure 1.6.4). Typically, the line of best fit should have as many points on the line as possible, but if this is not possible then it should have as many points above the line as there are below the line. The position of this line can be estimated by eye, but mathematical or graphing programs can be used to determine the line of best fit more accurately.

The line of best fit is a straight or curved that best summarises the general pattern of the data on the graph.

Graph showing an example of a line of best fit

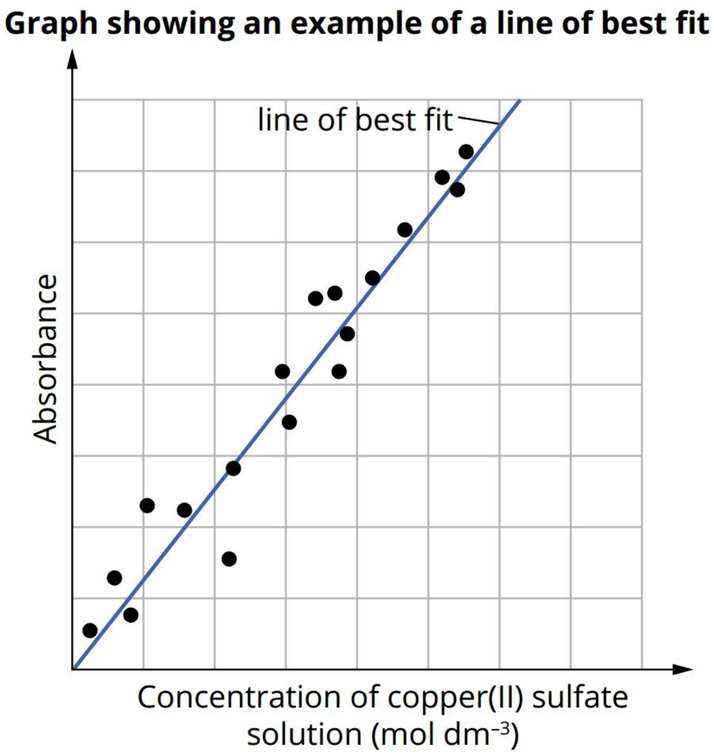


FIGURE 1.6.4 This graph shows that the line of best fit should summarise the data rather than pass through each point. It should be extrapolated so that it intersects the *y*-axis.

These are some of the general rules to follow when making a graph.

- Keep the graph simple and uncluttered.
- Use a descriptive title.
- Represent the independent variable on the *x*-axis and the dependent variable on the *y*-axis.
- Start each axis at zero.
- Match the length of the axes to the data.
- Clearly label each axis with both the variable and the unit in which it is measured.
- Use small symbols such as circles or crosses for data points.
- Use different symbols or colours for different data sets.

TYPES OF GRAPHS SEEN IN CHEMISTRY

There are several types of graphs, including line graphs and bar graphs. The best one to use will depend on the nature of the data. In chemistry, many relationships exist between two variables and are represented as formulas and graphs. Each of the following graphs shows some particular relationship between the independent and dependent variables that occur often in chemistry.

You will encounter all of these types of graphs at some stage during your Chemistry course.

Scatter plots and line graphs

Scatter plots are commonly used to display data in the form of a graph, and can be used to plot raw or processed data. They are used to show the relationship between two variables when one variable is dependent on the other.

The independent variable, which is set by the experimenter, is always shown on the *x*-axis. The dependent variable, which is the variable measured in the experiment, is always shown on the *y*-axis. The data is plotted on the graph as a series of points. Each point should be drawn in pencil as a small circle or cross. Alternatively, you can use a computer program to generate your graphs.

A **line graph** is a good way of representing **continuous quantitative data**. In a line graph, the values are plotted as a series of points on the graph. A line can then be drawn from each point to the next, as shown in Figure 1.6.5. This line shows the change in data from one point to the next, but does not predict the value of a point between the plotted data.

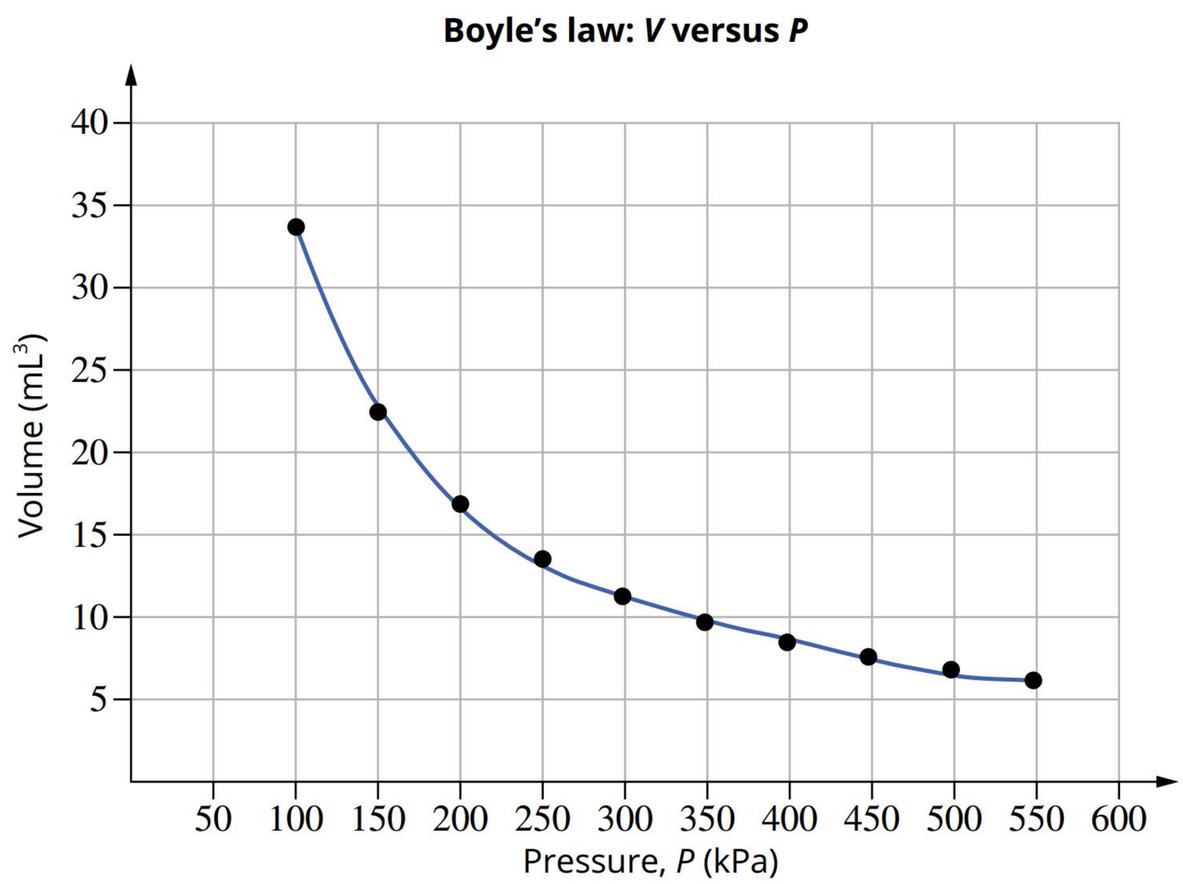


FIGURE 1.6.5 A line graph showing the change in volume of a gas in a syringe against the pressure of the gas inside

Alternatively, a line of best fit can be drawn as a single straight or curved line, as shown in Figure 1.6.6, which is also known as a **trendline**. It is used to show the overall trend in the data, and can be used to predict values between the data points. This will be covered in more detail in Module 1.7.

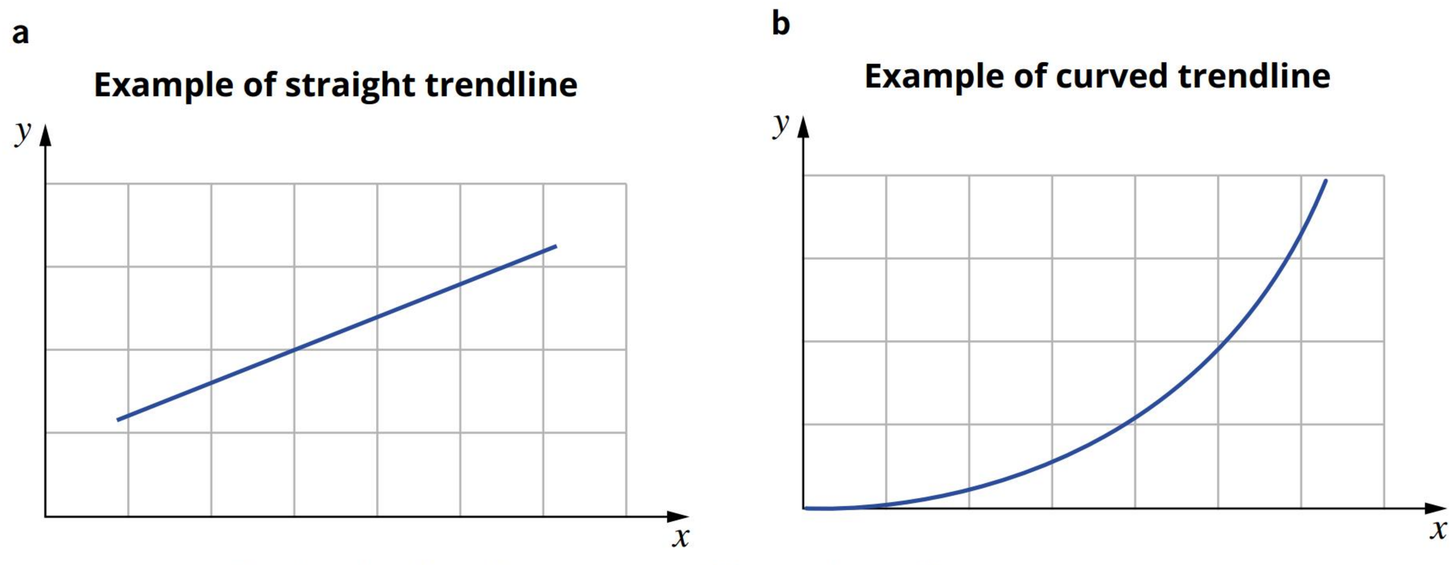


FIGURE 1.6.6 Graphs showing (a) straight and (b) curved trendlines

Bar and column graphs

Bar and column graphs are used to show categories and **discrete (discontinuous) data**.

- A **column graph** shows the value of the dependent variable by the height of the column; the categories are labelled across the *x*-axis.
- A **bar graph** shows the value of the dependent variable by the length of the horizontal bar; the categories are labelled up the *y*-axis.

Bar and column graphs are commonly used when the independent variable is categorical rather than numerical, or when the numerical data is discrete. The bars or columns are always the same width and the same distance apart.

Bar and column graphs are very useful for graphing qualitative and discrete data, such as the water quality data from various locations along a waterway (Figure 1.6.7).

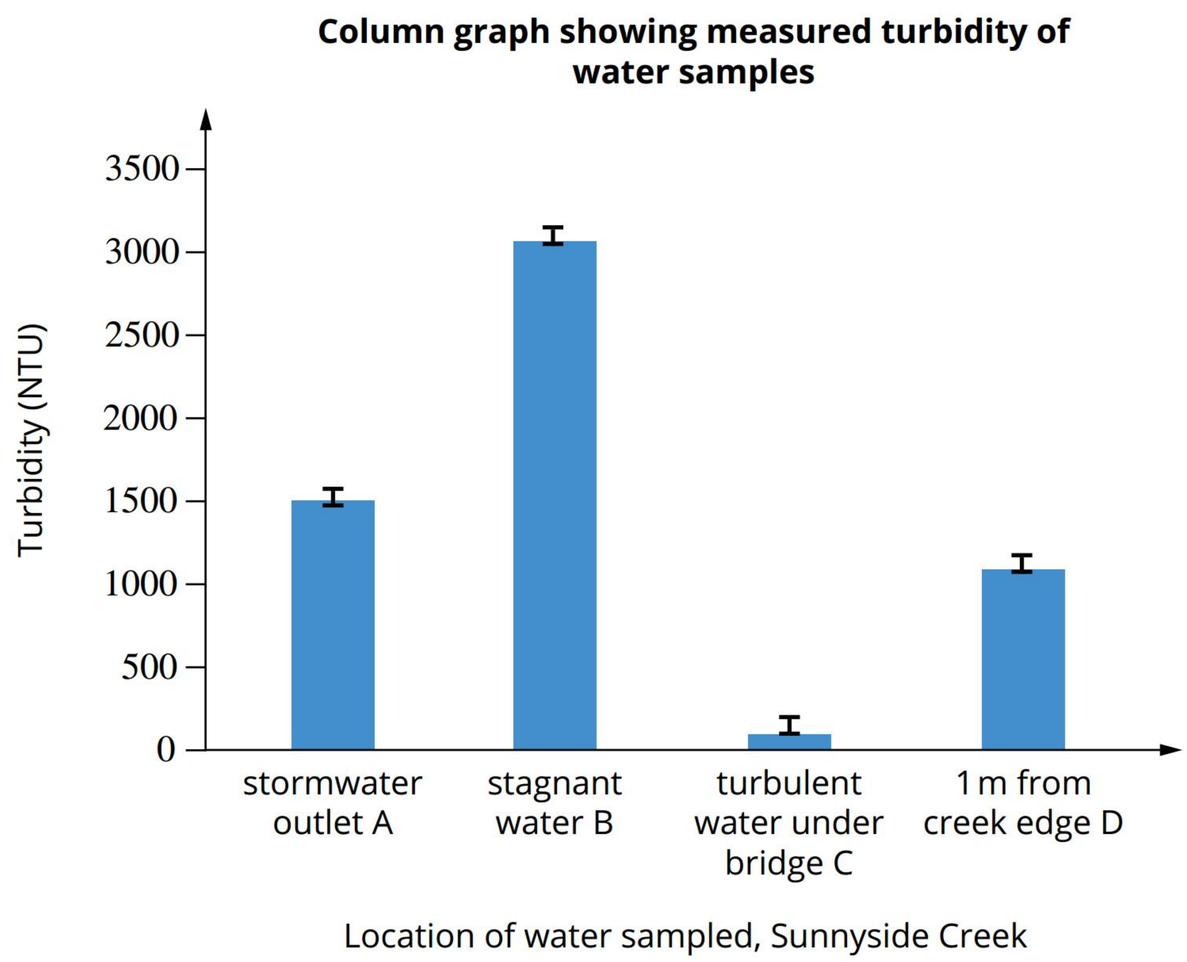


FIGURE 1.6.7 A column graph can be used to compare data. This graph shows the measured turbidity of water samples taken from various locations along Sunnyside Creek. Error bars show the uncertainty in the turbidity measurements.

OTHER GRAPHING CONSIDERATIONS

Missing data

When you have missing data, leave a gap for it, as shown in Figure 1.6.8. Ensure that the axes are complete (do not skip values) and do not join the data points that have missing data points between them.

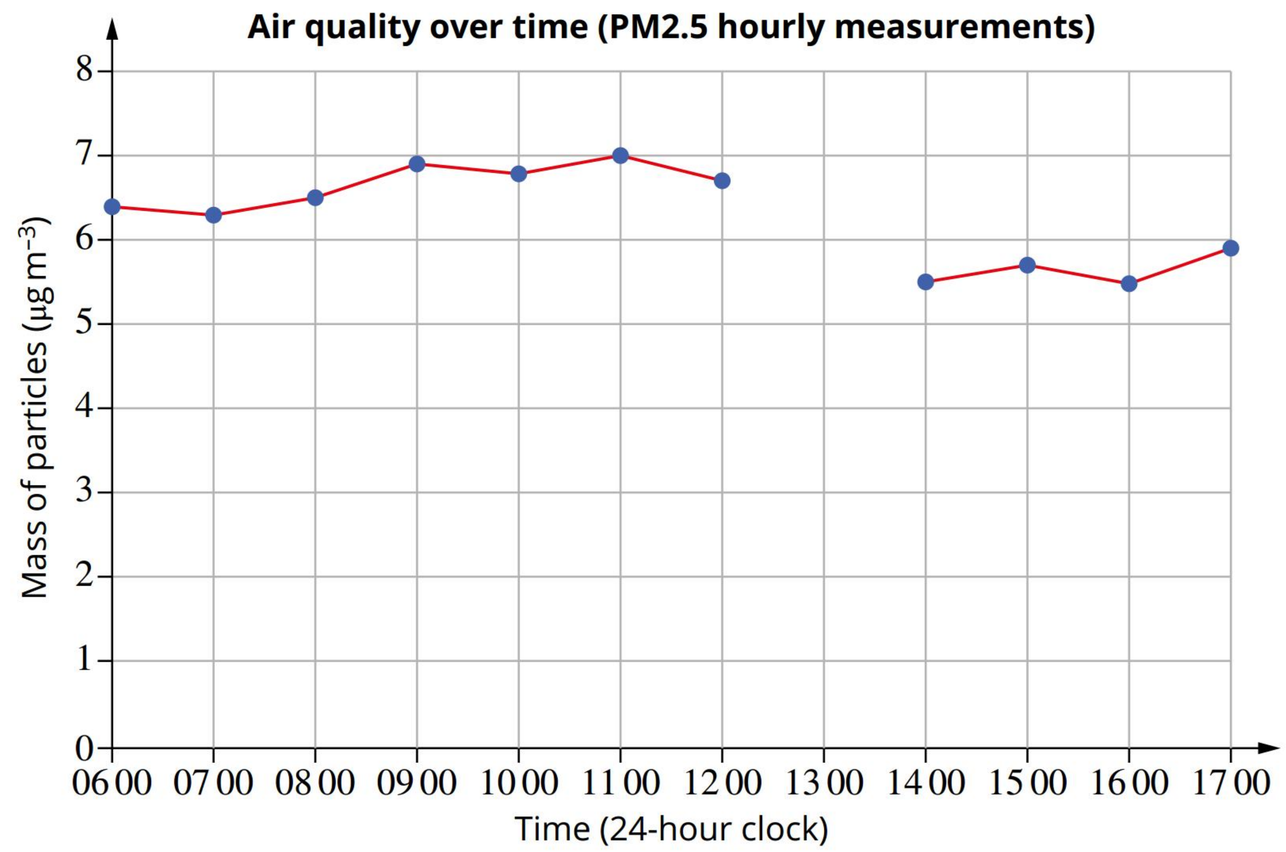


FIGURE 1.6.8 A line graph with data missing (for 1300)

Outliers

Sometimes when you collect data, there may be one point that does not fit the trend and may be an error. This is called an **outlier**. An outlier is often caused by a mistake made in measuring or recording data, or from a random error in the measuring equipment. This is covered in more detail later in this module. If you have an outlier in your results, you include it in your graph but ignore it when drawing the line of best fit, as shown in Figure 1.6.9 where the point (0.48, 0.08) is an outlier.

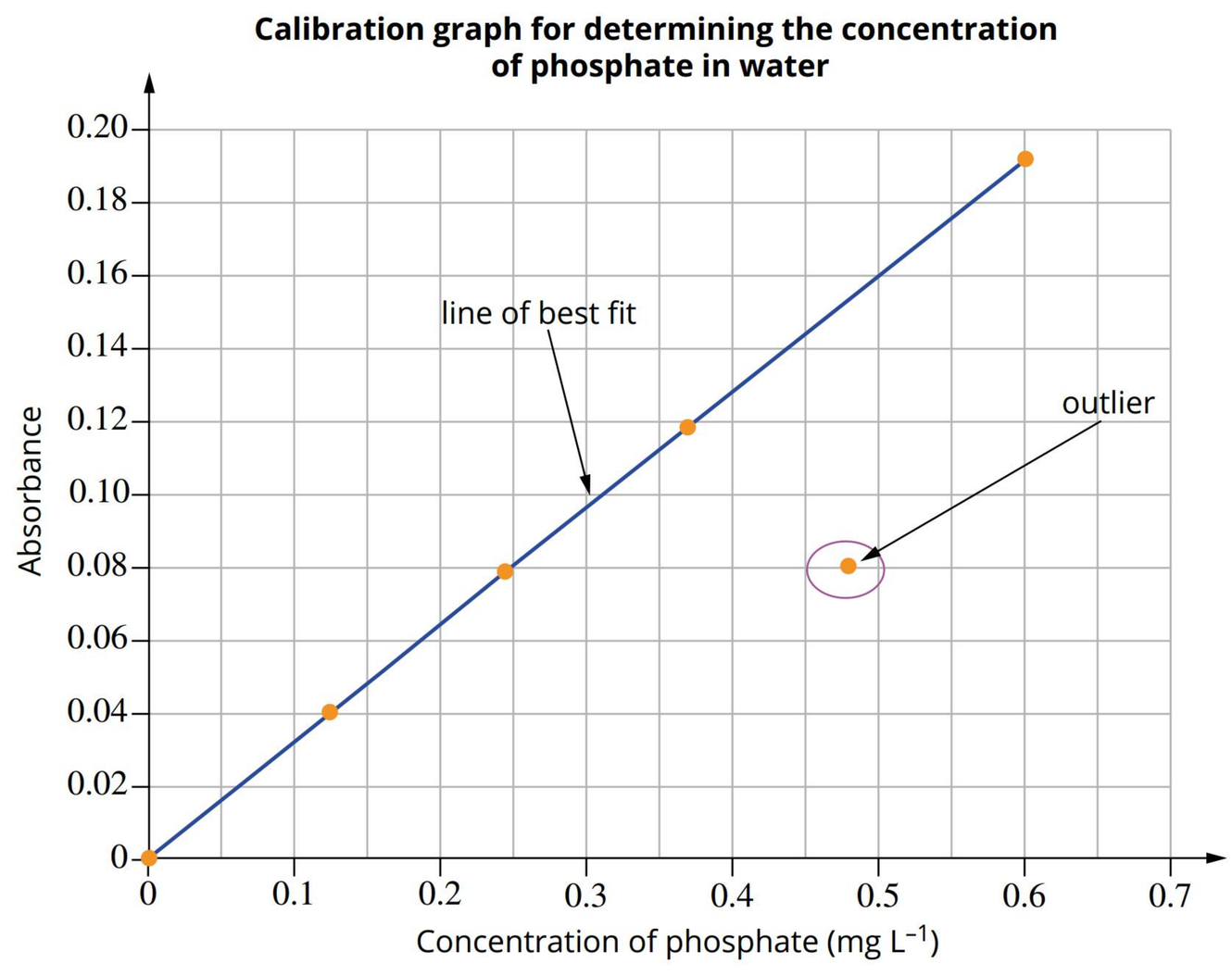


FIGURE 1.6.9 The graph is a calibration graph for determining the concentration of phosphate in water. A line graph shows an outlier, which has been ignored when adding the line of best fit.

Distorting the truth

Poorly constructed graphs can distort the truth. For example, in Figure 1.6.10, you can see two graphs that show the same data—the test results of two groups of students. One group of students did not eat breakfast before doing the test and scored an average of 42 marks out of 50. The other group of students did eat breakfast and scored an average of 48 marks out of 50. Figure 1.6.10b distorts the difference in marks between the two groups by using a scale that only ranges from 40 to 50 marks on the *y*-axis. It is important to make sure the graphs you create do not distort your data. You should also be wary of distorted data when interpreting graphs in other publications.

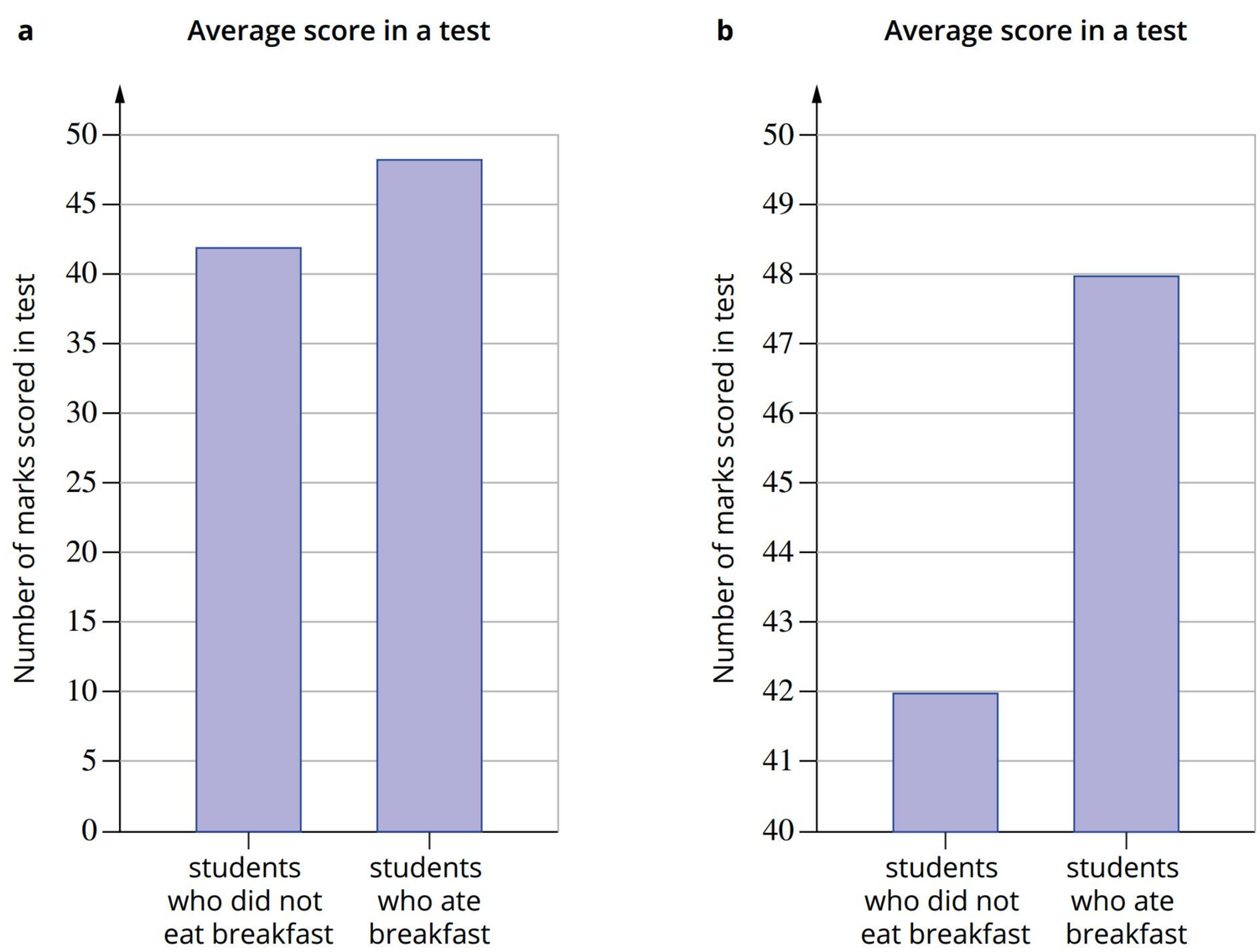


FIGURE 1.6.10 (a) The difference in the average scores between two groups of students (out of the maximum score of 50 marks) on the *y*-axis. (b) The difference between the two groups within only a narrow range of marks on the *y*-axis, which distorts the difference and makes it appear larger than it really is.

1.6 Review

SUMMARY

- Tables and graphs are used to represent scientific data.
- In general, tables provide more detailed data than graphs, but it is easier to observe trends and patterns in data in graph form than in table form.
- Tables organise data into rows and columns, and can vary in complexity according to the nature of your data.
- Tables should have the following features:
  - a descriptive title
  - column headings (including the units)
  - aligned figures (align the decimal points)
  - the independent variable placed in the left columns
  - the dependent variable placed in the right columns.
- Graphs are used to display relationships, trends and patterns between two variables with one proposed to be dependent on the other.
- There are several types of graphs, including line graphs and bar graphs. The best one to use will depend on the nature of the data.
- Scatter plots are commonly used to display data in the form of a graph, and can be used to plot raw or processed data.
- A trendline (line of best fit) is used to show the overall trend in the data, and can be used to predict values between the data points.
- A line graph is a good way of representing continuous quantitative data.
- Bar and column graphs are used to show categories and discrete (discontinuous) data.
  - A column graph shows the value of the dependent variable by the height of the column; the categories are labelled across the *x*-axis.
  - A bar graph shows the value of the dependent variable by the length of the horizontal bar; the categories are labelled up the *y*-axis.
- Missing data are represented in graphs by leaving a gap.
- An outlier are a data point that does not fit the trend, and may be caused by an error.

KEY QUESTIONS

Describe

1 State the purpose of a trendline.

Apply

2 Explain what outliers are.

3 Identify the relationship between the variables indicated by a sloping linear graph.

4 Explain how the general pattern (trend) of a graph can be represented once the points are plotted.

Analyse

5 Antonia draws a straight-line graph of data, including error bars, from an experiment she has just completed. She finds that it is not possible to draw a straight line of best fit through every error bar. Analyse the problem and advise Antonia on what to do.

6 If a theory suggests that the *y*-intercept of a line is zero, deduce what this should look like on a linear graph.

7 Assess when it is more appropriate to use a graph showing a line of best fit rather than a ruled line graph that joins each point.

8 Consider the data below and determine the relationship between atmospheric pressure and altitude.
Describe the trend and draw a graph, including a line of best fit.

Pressure (atm)	1.00	0.79	0.52	0.23	0.11	4.5×10^{-2}	1.3×10^{-2}	6.0×10^{-3}	2.1×10^{-3}
Altitude (km)	0	2.0	5.0	10.0	15.0	20.0	30.0	40.0	50.0

1.7 Data analysis

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- calculate and interpret the range, mean, median and mode of a set of data
- use the R^2 values to evaluate the fit of a trend to a set of data.

One of the difficulties in chemistry is that direct measurements of phenomena or measurements within a closed system are challenging to obtain. Therefore, the limitations and uncertainty in the data include uncertainties in the accuracy and precision of the measurements that were recorded, as well as errors related to reliability and validity of the experimental procedure. To address this problem, chemists perform statistical analysis to help understand the quality of the measurements, the results and their meaning.

This module will outline a basic understanding of common statistical analysis used in chemistry relevant to the Chemistry General Senior Syllabus.

STATISTICAL MEASURES

There are a number of common statistical measures that help describe data accurately.

Range

The range is the difference between the highest and lowest values in a data set. Table 1.7.1 shows the measurements taken for a reaction between sodium thiosulfate and sulfuric acid.

TABLE 1.7.1 Time for the reaction mixture to turn opaque in the reaction between sodium thiosulfate and sulfuric acid at 20°C and 50°C

Temperature	1	2	3	4	5	Mean	Range
20°C	253	158	201	169	187	193.6	253 – 158 = 95
50°C	69	85	70	91	75	78	91 – 69 = 22

To determine the range for values in Table 1.7.1, you would subtract the smallest value from the largest value. Notice how an abnormally large or abnormally small value in the data set makes the variability appear high. If one value appears way out of range, such as the time taken for the reaction mixture to turn opaque for the first time the reaction was performed at 20°C, it may be an outlier. This illustrates the importance of observation during experiments and recording all details in a journal as experimentation and research is conducted.

The experiment was conducted with a smaller number of measurements taken at each temperature, and the results are shown in Table 1.7.2.

TABLE 1.7.2 Time for the reaction mixture to turn opaque in the reaction between sodium thiosulfate and sulfuric acid at 20°C and 50°C

Temperature	1	2	3	Mean	Range
20°C	253	158	201	204	253 – 158 = 95
50°C	69	85	70	74.6	85 – 69 = 16

Even though the range has not changed much between Tables 1.7.1 and 1.7.2, the results at 20°C seem more random. In Table 1.7.2 at 50°C, the second reaction could be an outlier as the other two results show excellent agreement. The range simply outlines the total variation in measured results; no other analysis or interpretation can be achieved.

A larger **sample size** will strengthen the **validity** of the range.

Measures of central tendency

Measures of central tendency (also called central location) are single values that allow you to describe the central position in a set of data. The mean, median and mode are all measures of central tendency.

Consider the following data set: 3, 5, 7, 8, 8, 8, 10.

- The **mean** (or average) is the sum of the values divided by the number of values, which in this case is (3 + 5 + 7 + 8 + 8 + 8 + 10) ÷ 7 = 7.

$$\text{mean} = \frac{\sum(x_1 + x_2 + x_3 + \ldots)}{n}$$

where $\sum$ = sum of

$x_1 + x_2 + x_3 + \ldots$ = measurement$_1$ + measurement$_2$ + measurement$_3$

n = total number of measurements

- The **median** is the 'middle' value in an ordered list of values, which in this case is the fourth value, which is 8.
- The **mode** is the value that occurs most often in a set of values, which in this case is 8. This measure is particularly useful for describing qualitative or discrete data.

The appropriate measure of central tendency to use depends on the type of data you are working with (Table 1.7.3).

TABLE 1.7.3 When to use the different measures of central tendency

Type of data	Mean	Median	Mode
nominal (qualitative)	✗	✗	✓
ordinal (qualitative)	✗	✓	✓
discrete or continuous (quantitative)	✓	✓	✓

Graphically representing the data using central tendency provides a clear and succinct display of results. As there are many measured values and results in raw data, it can be difficult to analyse and interpret. It is much easier and less complicated to analyse and interpret processed data compared to raw data. Raw data includes all the measured results, and usually a large number of measurements or observations.

Processed evidence is usually a smaller number of results that represent all the measured raw data; these representative results are calculated using statistical methods such as mean, median and mode. Therefore, an analysis can be conducted to compare fewer results (e.g. two means) rather than comparing all the individual measurements in a set of raw data. Interpreting a relationship between variables is also much easier and less complicated when using fewer numbers.

It is important to realise that statistical calculations do not produce the true value, but rather a single value (or smaller number of values) that is meant to represent many. Analyse the mass of two alcohols burnt in a calorimetry experiment, shown in Table 1.7.4. The average has been calculated for each alcohol; however, you will notice that the mean value was not measured during the experiment and is not in the raw data.

TABLE 1.7.4 Mass of ethanol and hexanol burnt

Ethanol (g)	Hexanol (g)
0.77	1.60
0.78	1.82
0.72	1.67
0.73	1.72
0.76	1.71
0.74	1.80
Mean 0.75	Mean 1.72

REGRESSION

Regression is the term used to describe the degree to which the independent variable causes the change in the dependent variable during a scientific investigation. Some relationships between variables are causal, meaning that there is a cause-and-effect relationship. The independent variable is the cause and the dependent variable is the effect.

There are numerous statistical calculations that estimate the causal relationship between variables. Some calculations provide a value that indicates how directly an independent variable affects the dependent variable. This attempts to show the strength of the relationship, and to identify if the change in the dependent variable is entirely due to the independent variable.

In chemistry, not all relationships are direct or straightforward cause-and-effect. Often there are many variables that influence the dependent variable and it is helpful to try and predict how much of an effect the independent variable has on the dependent variable, even when other variables are also influential.

Coefficient of determination (R^2)

The **coefficient of determination** (R^2) produces a value that is an estimate as to how well you can predict the dependent variable based on the independent variable, considering the variations in the results. In the examples in Figure 1.7.1, the data for technique 1 does not follow the linear trendline exactly; therefore, as the concentration changes (the independent variable), the absorbance (the dependent variable) does not always change consistently. The coefficient of determination is a calculation that considers the variation in the results to estimate the predictability.

For example, a laboratory has used two different analytical techniques to determine the concentration of a performance-enhancing drug in a blood sample from an athlete suspected of cheating. The calibration curves for each technique and the R^2 value for each technique are shown in Figure 1.7.1.

Based on the lines of best fit and R^2 values, the second method was chosen to analyse the athlete's blood sample.

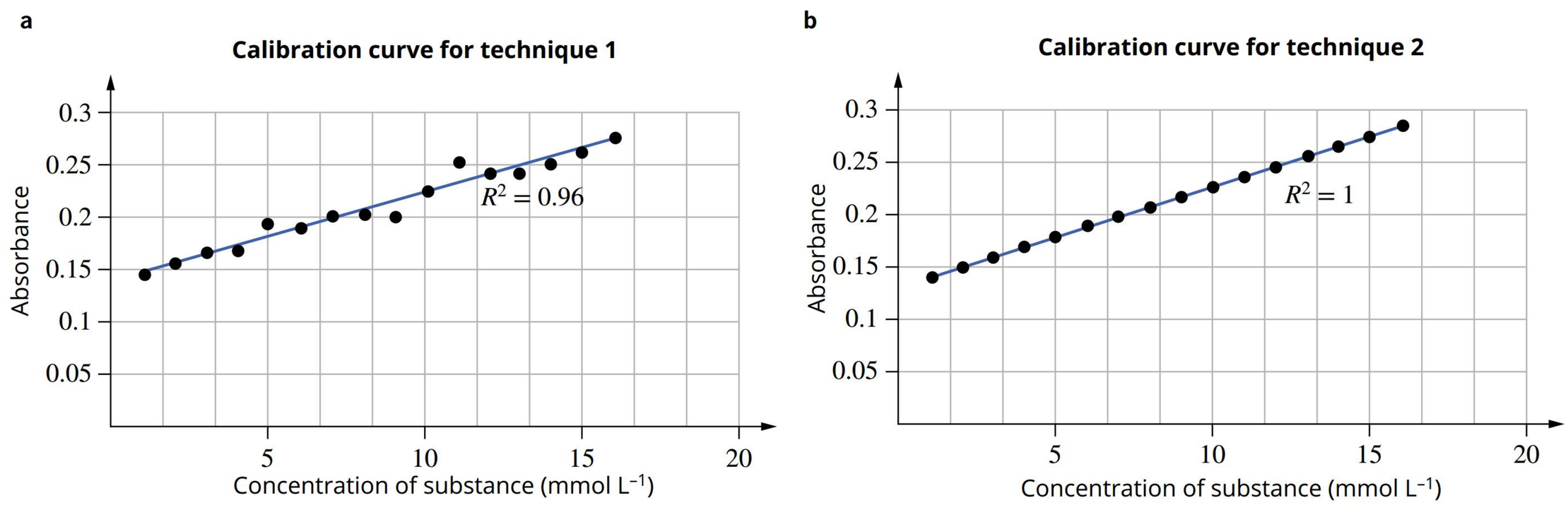


FIGURE 1.7.1 (a) The calibration curve for technique 1: linear regression was used to establish a line of best fit. (b) The calibration curve for technique 2: linear regression was used to establish a line of best fit.

Even though both techniques measured the same samples, the data is different. As can be seen in the graphs, the linear trendline has a similar slope; however, technique 1 has an R^2 value of 0.96, and for technique 2, it is 1.00.

The coefficient of determination produces a value between 0 and 1. If the value is 0, it is unable to predict the change in the dependent variable from the independent variable due to so much variation in the results. If the value is 1, then it can predict the change in the dependent variable 100% of the time without error. Any other number between 0 and 1 is considered a percentage; for example, 0.76 means that the coefficient of determination can predict 76% of the dependent variable results due to change in the independent variable. It is interpreted as: 76% of the variation in the dependent variable can be explained by the independent variable.

In Figure 1.7.1b, the absorbance of the sample was perfectly correlated without error with the concentration of the species. This suggests that the results from technique 2, including error, **bias** and instrumental precision, are highly reliable.

Figure 1.7.1a shows that the absorbance of the sample was not precisely correlated with the concentration. The R^2 value for technique 1 is lower than for technique 2, meaning the results are less predictable due to more variation. Technique 1 was less precise compared to technique 2; therefore, technique 2 is the preferred technique to determine the concentration in the actual sample.

1.7 Review

SUMMARY

- The range is the difference between the highest and lowest values in a data set.
- The mean, $\bar{x}$, is the average of a data set. It is calculated using the formula:

  $\bar{x} = \frac{\sum x_1 + x_2 + x_3 \ldots}{n}$, where

  $\sum$ = sum of

  $x_1 + x_2 + x_3 + \ldots$ = measurement$_1$ + measurement$_2$ + measurement$_3$

  n = total number of measurements.
- The median is the 'middle' value in an ordered list of values.
- The mode is the value that occurs most often in a data set. The mode is particularly useful for describing qualitative or discrete data.
- Regression is the term used to describe the degree to which the independent variable causes the change in the dependent variable during an experiment.
- Linear regression is a calculation that estimates a direct linear relationship between the independent and dependent variables.
- The coefficient of determination estimates how well you can predict the dependent variable based on the change in the independent variable.
- The coefficient of determination produces an R^2 value between 0 and 1.
  - The closer the R^2 value is to 0, the less predictable the dependent result is based on the independent value.
  - The closer the R^2 value is to 1, the more predictable the dependent result is based on the independent value.

KEY QUESTIONS

Describe

1 Define the terms 'mean', 'median' and 'mode'.

Apply

2 Explain why a coefficient of determination, R^2, cannot be greater than 1.

Analyse

3 For the data set {21, 28, 19, 19, 25, 24, 20}, calculate the:

a range

b median

c mode

d mean

4 Identify which of the statistical measurements of mean, mode and median is generally most affected by an outlier.

1.8 Scientific writing

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- use scientific language and representations
- use a scientific journal for experiments
- reference sources and avoid plagiarism
- use and reference AI in research and writing
- communicate findings in a multimodal presentation.

The QCAA requires students to complete a student experiment as part of Unit 3 Chemistry and a research investigation in Unit 4 Chemistry. Both tasks require written or multimodal presentations. Preparing and presenting scientific reports and investigations involves research and note-taking skills, use of scientific genre, language and representations and referencing knowledge to acknowledge sources used.

Scientists follow strict genre conventions when undertaking and communicating their work. These are described in this module. Refer back to this module as you complete the student experiment and research investigation.

SCIENTIFIC WRITING AND REPRESENTATIONS

Scientific reports must be written using scientific language and representations—these should be relevant, fluent and concise. To meet the word count or time requirements, use only the words required to communicate your information and avoiding repetition. Having a plan and using a journal also helps to achieve fluent and concise writing. Use the syllabus objectives, specifications and the instrument-specific marking guide (ISMG) to plan an outline of each section of your written task.

Table 1.8.1 demonstrates communication of the same concept in a few different ways. Being fluent and concise will significantly influence the word count of the report and the quality of the writing.

TABLE 1.8.1 Communicating concepts in various ways

Concept	Communication	Commentary of communication
the basic structure of an atom	An atom is made up of protons, neutrons and electrons.	This is fluent and concise, but lacks scientific terms or language to convey in-depth understanding.
	Atoms are tiny little objects made up of numerous parts that form the basis of matter. Atoms are made up of electrons, neutrons and protons. The electrons are found away from the centre of the atom. The centre of the atom contains the protons and neutrons.	This is fluent, but not concise. There is repetition (e.g. 'tiny' and 'little'—these terms have the same meaning; also 'made up' is stated twice). It also uses many words without using scientific terms to provide detail and understanding. This may be useful language in the journal when learning about a topic, but not in the scientific report.
	Atoms are particles composed of three types of subatomic particles: protons, electrons, and neutrons. The centre of an atom is the nucleus and contains the protons and neutrons, with the electrons occupying space external to the nucleus.	This is fluent and concise. Much in-depth understanding is communicated through scientific terms, which enable much information to be conveyed in fewer words.

Reports are written using paragraphs, with each paragraph explaining only one idea. The first sentence (topic sentence) of the paragraph introduces the topic. Following sentences provide the details of the idea. The final sentence concludes the idea and may also link to the idea of the next paragraph. Each sentence should flow onto the next, slowly building the details of the explanation.

Reports should be written using:

- past tense—as the experiment was conducted in the past, the report should be in the past tense
- third person, passive voice and impersonal verbs—science uses this language convention (Table 1.8.2)
- scientific language—the terms used are specific to concepts, models and theories
- information from secondary sources, which is written in your own words
- objective, unbiased language—avoid subjective and emotional or persuasive writing (Table 1.8.3)
- concise language—avoid unnecessary repetition and express ideas clearly. Scientific language allows more details, knowledge and understanding to be communicated in fewer words. Use shorter sentences that are less wordy (Table 1.8.4)
- headings and subheadings can be used to break up a report.

Table 1.8.2 shows some examples of more concise wording.

TABLE 1.8.2 Examples of first-person and third-person narrative

First person	Third person
I put 50 g of marble chips in a conical flask and then added 10 mL of 2 M hydrochloric acid.	*First, 50 g of marble chips was weighed into the conical flask, and then 10 mL of 2 M hydrochloric acid was added.*
After I observed the reaction, I found that …	*After the reaction was completed, the results showed …*
My colleagues and I found …	*Researchers found …*

TABLE 1.8.3 Persuasive writing versus scientific writing styles

Persuasive writing examples	Scientific writing equivalent examples
Biased and subjective language: *The results are extremely bad/atrocious/ wonderful, etc.* *This is terrible because …* *This produced a disgusting odour.* *Health crisis!*	Unbiased and objective language: *The results showed …* *The implications of these results suggest …* *The results imply …* *This produced a pungent odour.* *Health issue*
Exaggeration: *The object weighed a colossal amount, like an elephant.*	Non-emotive language: *The object weighed 256 kg.*
Use of everyday or colloquial language: *The bacteria passed away.* *The results don't …* *The researchers had a sneaking suspicion …*	Use of formal language: *The bacteria died.* *The results do not …* *The researchers predicted/hypothesised/ theorised …*

TABLE 1.8.4 Examples of verbose and concise writing

Verbose writing	Concise writing
Due to the fact that …	*Because …*
Smith undertook an investigation into …	*Smith investigated …*
It is possible that the cause could be …	*The cause may be …*
end result …	*result …*
In the event that …	*If …*
shorter in length …	*shorter …*

To produce a fluent report, the scientific language must be used without error so that the reader understands the meaning of the information easily. Refer to the syllabus for the correct scientific terminology. For the report to be concise, there should not be any repetition. Being fluent and concise will significantly influence the word count and the quality of writing. Refer to the syllabus ISMG to identify the cognitive verbs used in the descriptors to produce the appropriate response. For example, you will need to write more extensively if you are asked to 'discuss' or 'explain' compared to 'identify'.

Scientific representations

Chemical structures, equations and diagrams are an efficient way of presenting complex data and explaining chemical concepts. Flow charts, graphs, tables and photographs are also used. Ensure you include:

- a descriptive title
- labels, captions or descriptions
- numbering; for example, Figure 1, Figure 2, etc., or Table 1, Table 2, etc.
- a source if the work is not your own or is adapted from work that is not your own.

SCIENCE JOURNAL

There is a lot of information to record during the student experiment or research investigation, so it would be best to keep a **scientific journal**. Entries in your journal should include the following features:

- the date of entry
- ideas, observations, proposals, questions
- background information you researched for the task
- new terms and definitions
- refinements
- results, data, evidence, variables
- explanations, ideas, observations (including diagrams)
- limitations, conclusions, further investigation.

A journal holds a record of information used during the process of the scientific method (Figure 1.8.1 on page e56). You will not know what is vital information until your experiment is complete and summarised into the scientific report. Data and graphs may be saved digitally, so reproduce a sketch in your journal that you can annotate with your thoughts. You may choose to prepare a page or two each for the four key sections of the task (e.g. for IA2: Forming, Finding, Analysing, Interpreting and Evaluating) or use proposed report headings (e.g. Rationale, Research Question, etc.).

Researched and recorded information in your journal will be used for the Rationale, to justify the modifications to the methodology, to provide a reason for collecting data, to inform risk, ethical and environmental management, and to collate and process the data. It will also inform the interpretation of the evidence (results) and conclusion. Remember, parts of the Rationale (planning) and the data collection are completed with your group and shared—the rest of the task is individual and so is your journal. A journal is not an assessed part of the task, but will likely be reviewed by your teacher as a progress check and to confirm that the work is yours. Depending on the size of the journal, it may be copied and attached in the Appendix of your report.

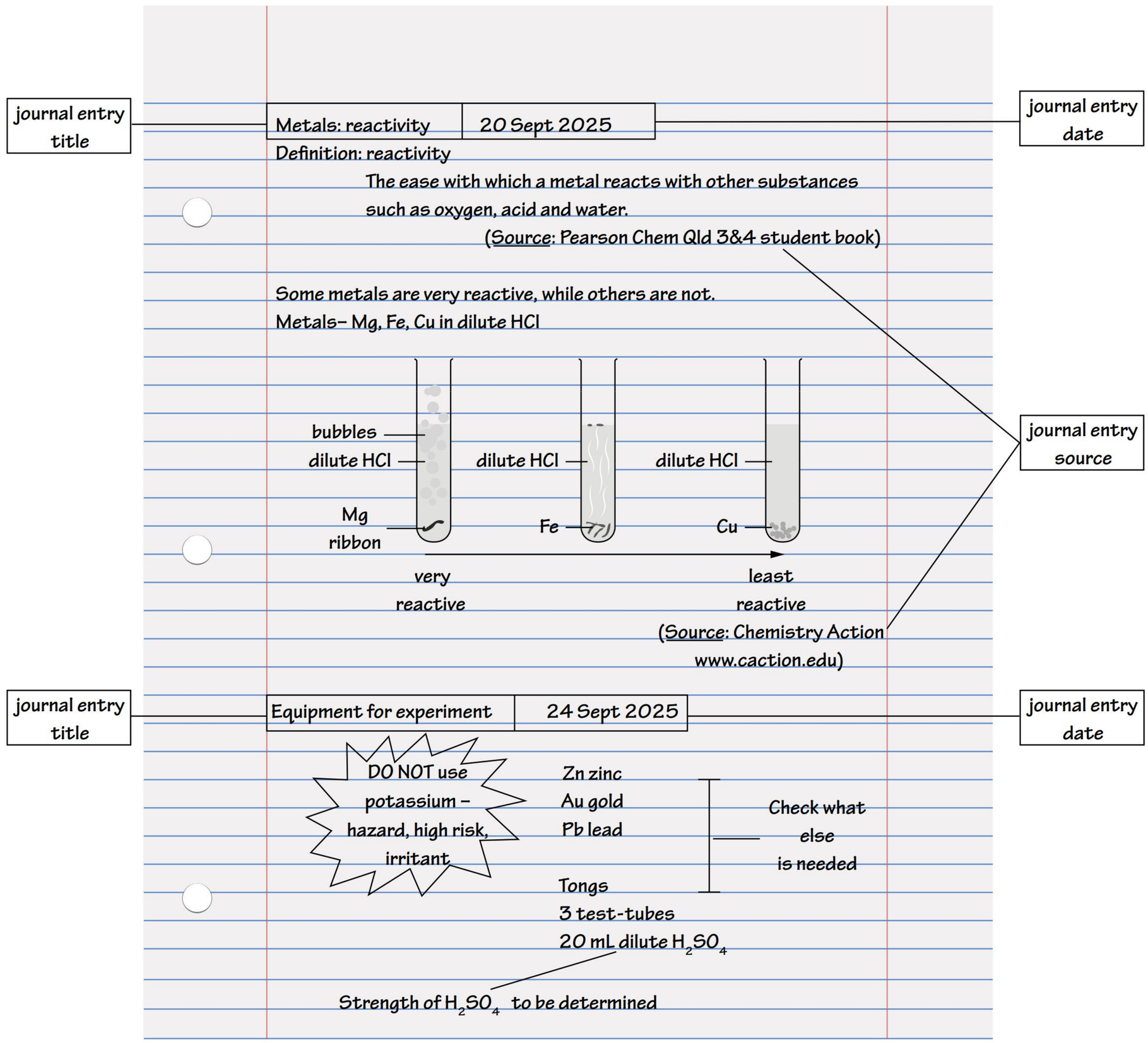
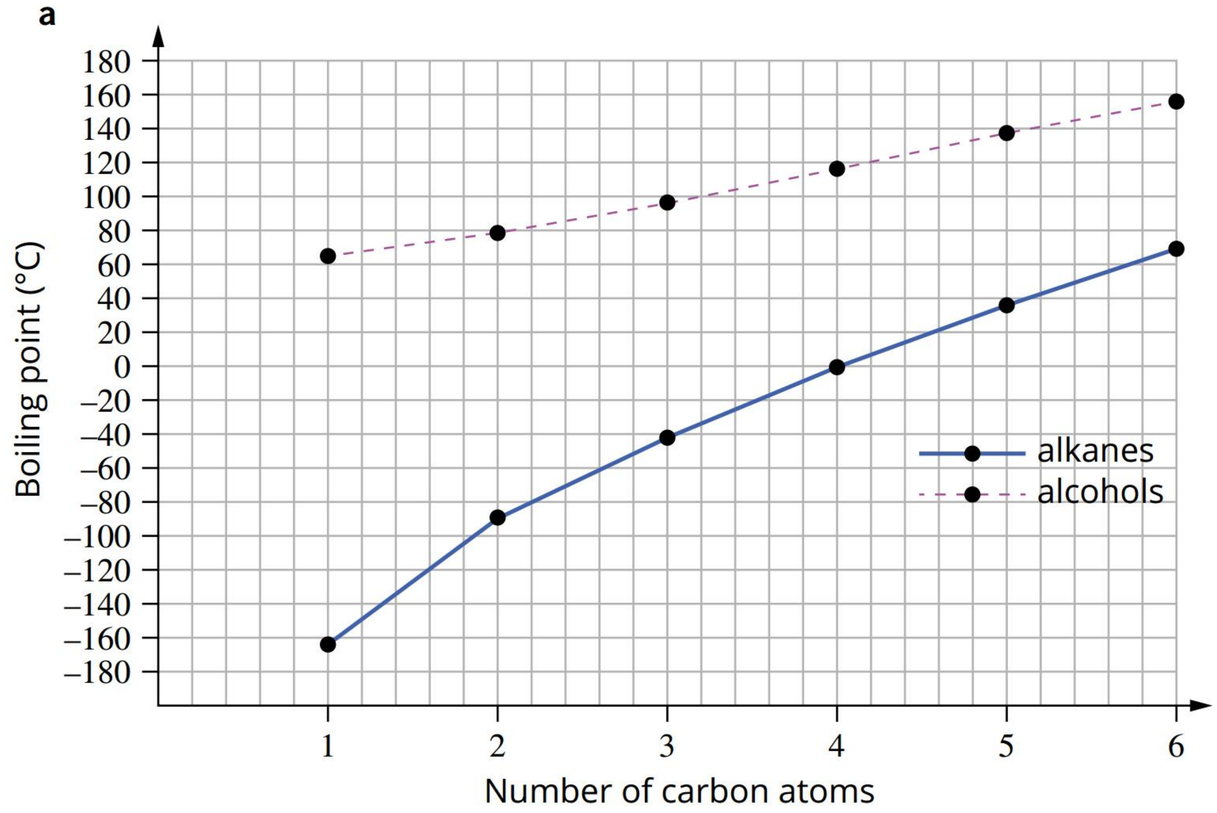


FIGURE 1.8.1 Journal entries with the journal entry date, title and apparatus used in preparation for an experiment. There will be numerous journal entries on any given date, and each should have its own title. The same titles will appear on different entry dates as research continues on specific topics.

Journal entries can take different formats. Sometimes one form of recording information provides more details than others. Note taking is not limited to words. Figure 1.8.2 presents the same information in different ways.

a



b

The boiling points increase with increasing number of carbon atoms. This indicates that the intermolecular forces that are being broken during boiling are getting stronger.

The intermolecular bonds between alcohol molecules are stronger than those in alkane molecules that contain the same number of carbon atoms.

The difference in electronegativities between the oxygen and hydrogen atoms creates a polar bond, which means that the intermolecular bonds stronger – forms H bonds compared to the temporary dipoles in alkanes, as the electronegativities of carbon and hydrogen atoms is much less.

The gap between each line is decreasing.

c

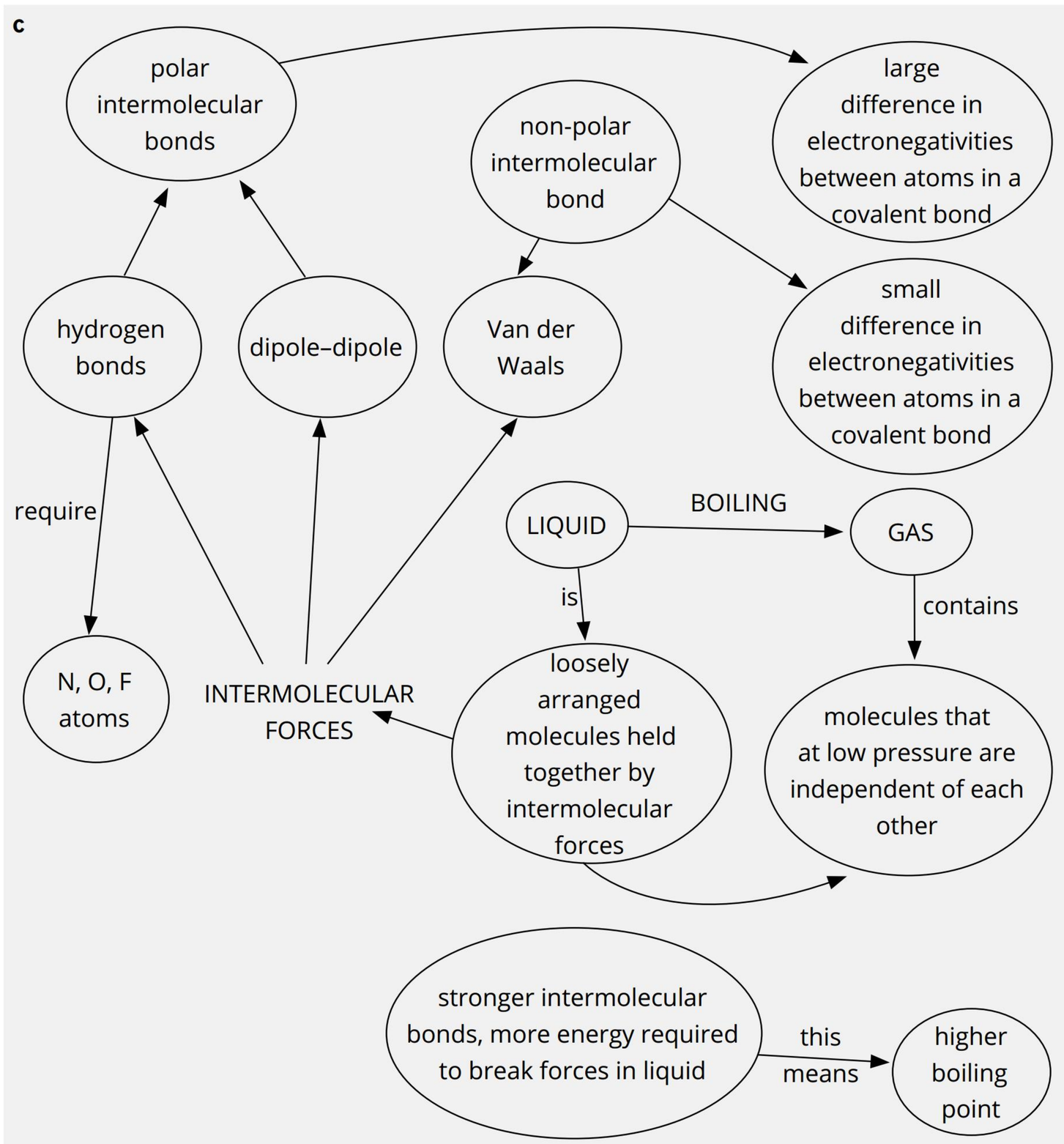
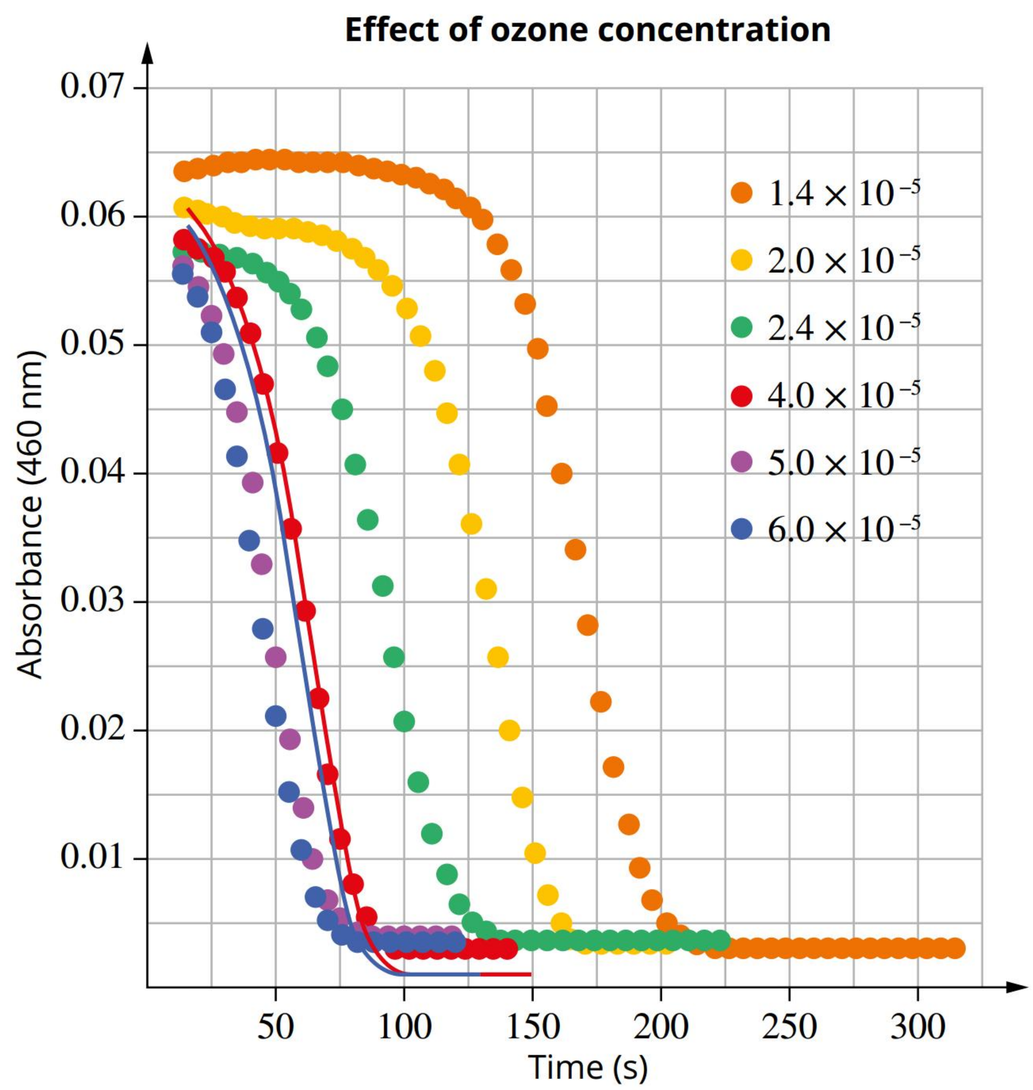


FIGURE 1.8.2 (a) Graphical representation of the boiling-point trend for alcohols and chain alkanes. (b) Written comparison of the boiling-point trend. (c) Concept map linking electronegativities of atoms to the boiling points.

When recording results, data or evidence in your journal, be critical and interpret the data as it is collected. In this way, errors in the method are identified or the sample size can be adjusted, if needed. If a given group member has the recording task, it is vital that the data set is passed to all group members before leaving the laboratory. Add this information directly into your journal and annotate with your own comments. Figure 1.8.3 shows an example of research evidence and how it is interpreted in a journal. Notes in your journal can also include:

- specific details and your interpretation of significant values
- the trend or pattern and a statement of whether this is the expected one
- the comparison or difference between one set of values and another
- the statistics used to establish the significance and the author's interpretation.



Effect of the ozone concentration on the clock time.
The initial concentrations after mixing the reactants in the cuvette were as follows:
$[O_3]$ as indicated in the figure (mol L^{-1})
$[NaClO_3]$ = 0.0251 mol L^{-1}
$[HClO_4]$ = 0.474 mol L^{-1}
$[I_2]$ = 8.8×10^{-5} mol L^{-1}.
Experimental data (symbols); modelling results (continuous line)

FIGURE 1.8.3 Example of interpretation of research evidence

REFERENCING SOURCES

When gathering scientific evidence for a scientific inquiry such as your student experiment and research investigation, source information from reputable publications such as:

- your student book and practical manual. This should be your first source of reliable information.
- scientific journals and magazines: research papers and scientific reviews. Common commercial science magazines that you might find in your school library include *Cosmos*, *Scientific American* and *New Scientist*. Scientific journals are peer-reviewed, which gives them credibility.
- podcasts and websites. Electronic sources include online scientific organisations such as CSIRO, NCBI, AIMS, Bioscience (Oxford Academic) and other university publications and press. In general, use websites that are .edu, .gov or .org. Many government and privately funded science organisations publish useful material, along with not-for-profit scientific organisations. Websites may direct you to magazines and scientific journals, podcasts, blogs and videos.

In the chemistry syllabus, you are asked to "discuss and evaluate the validity and reliability of evidence" (Science Inquiry skills). When selecting and using sources of information and evidence, follow these guidelines:

1 Confirm that it is relevant.
   - **a** Check that the evidence contains information that is specifically related to the inquiry.
   - **b** Check that the evidence and information are pertinent to the variables of the inquiry.
2 Assess its reliability.
   - **a** Is the evidence current or recent information?
   - **b** Is it correct in its understanding of relationships?
   - **c** Is the evidence in agreement with other sources?
   - **d** Check credibility and bias—consider who the author is, their qualifications, expertise and affiliations.
   - **e** Evaluate the methodology, including what variables were controlled or measured.

It is not necessary that each of your sources fulfil all of these requirements. Each source will have strong and weak points. For example, we are confident that information from a peer-reviewed scientific journal is unlikely to lack credibility or contain bias because the review process is undertaken by experts in the field. However, it may have been produced 10 years ago, so scientific information and relationships may not be up-to-date. Also, podcasts or science magazines for school students may contain a wide array of interesting real-world examples but may not explain the scientific understandings in sufficient detail. Some resources are available by paid subscription, so use advice from your school librarian about free resources or join your local library.

All quotations, documents, publications and ideas used in your investigation need to be acknowledged in the reference list in order to avoid plagiarism and to ensure creators are properly credited for their work. When using sources to explain chemical concepts or review data, ideas must be written in your own words (see Plagiarism, below). References and acknowledgements show that you have read widely, give credibility to your study and allow the reader to locate information sources should they wish to study it further.

Plagiarism

Plagiarism is using other people's work without acknowledging them as the author or creator. To avoid plagiarism, include a reference every time you report the work of others; for example, at the end of a sentence or following a diagram. If you use a direct quotation from a source, enclose it in quotation marks. This will ensure you give credit to the original author and it will enable the reader to find the original source.

Information taken from a source should be rewritten in your own words. It can be difficult to reword information in your own words. A useful strategy is to read the information, understand it and then, without looking back at the source, take notes in your journal. Notes that are detailed and have full explanations will be useful when you refer to them later to write the report.

TABLE 1.8.5 Suggestions for rewording information

Source information:	
"It can be expected that the days will be warm and the nights will be cool over the next three days due to the high-pressure system moving across the region."	
Strategy to change source information	**Reworded information**
The order of information can be swapped—the object (the warm days and cool nights) with the reason (high pressure system).	Due to the high-pressure system moving across the region, the days will be warm and the nights will be cool.
Some words can be changed, such as adverbs, nouns, verbs, adjectives.	It has been predicted that during the daytime it will be warm while the evenings will be cool for about three days, as a high-pressure system travels over the region.
Information can be elaborated to explicitly outline information.	The weather forecast expects (or, made a prediction based on computer simulations) that the temperature during the day will be warm (22–25°C) and the evenings will be cool (below 12°C) due the high-pressure system (or, weak high pressure system), which dissipates clouds and allows direct sunshine to warm the Earth's surface; however, in the evenings, this system brings cool air from higher altitudes, which is no longer warmed by the Sun.

Referencing

There are a number of different referencing styles, such as Harvard or APA. The sources of information must be acknowledged using a referencing style that is suitable for the purpose of the investigation. Check the preferred referencing style or convention of your teacher for in-text referencing and for compiling a complete **reference list**. APA style is the most commonly used referencing style. Reference examples are shown in Table 1.8.6.

A bibliography is a list of all the sources used during the research to develop understanding (including information in the journal) even if the information was not used directly or explicitly in the scientific report. A reference list only lists the sources used and cited (or in-text referenced) in the scientific report. As such, a reference list is the minimum requirement and you may choose to extend this to a bibliography. The sources must be listed at the end of the report in the style consistent with your style of referencing.

Compile all references you use both directly in the scientific report or in the gathering and development of the information in a separate document as you conduct the investigation. This will save you time later. Word processing programs, such as Microsoft Word® and other online tools, make writing a reference list easier by automatically formatting references in the referencing style of your choice. Always check that this tool has formatted references correctly.

TABLE 1.8.6 Examples of references

Books	Author surname then initials, year of publication, title, publisher.	Yurkanis Bruice, P. (2024), *Organic Chemistry*, Pearson. (one author) Natu, A. D., Bobade, V. D., & Gugale, G. S. (2019), *Organic Chemistry*, Nirali Prakashan. (more than one author)

In-text citations

Each time you write about the findings of other people or organisations, you need to provide an in-text citation and include full details of the source in a reference list. In the APA style, in-text citations include the first author's last name and date in brackets (author, date).

The following example shows two types of in-text citation and the reference list entry.

In-text citations
It was reported that in testing of five pro-oxidant additives added to commonly manufactured polymers, none resulted in significant biodegradation after three years (Selke et al., 2015).
Selke et al. (2015) reported that in testing of five pro-oxidant additives added to commonly manufactured polymers, none resulted in significant biodegradation after three years.
Reference list entry for the example above would be:
Selke, S., Auras, R., Nguyen, T. A., Aguirre, E. C., Cheruvathur, R., & Liu, Y. (2015), Evaluation of biodegradation—promoting additives for plastics. *Environmental Science & Technology*, 49(6), 3769–3777.

USING AI IN RESEARCH AND WRITING

Generative AI (or just AI) uses chatbots or digital assistants that you can communicate with to access information in Large Language Models (computer models trained on vast amounts of data). These typically generate text, and some models can generate images, video and audio.

AI can be great for brainstorming ideas about investigations, creating practice questions and generating data for investigations. However, you must follow guidance from your teacher or school on how you can use AI in your work. You could be penalised by your school for using AI-generated material without permission or acknowledgement. It is also important to understand the limitations of AI-generated content.

Limitations of AI-generated text

Large language models are engineered to match patterns of words, but they cannot understand the meaning of your prompt or the output text. They produce text that is similar to patterns of words in the prompts and outputs they have been trained on.

This can result in text that sounds knowledgeable and authoritative but does not mean much when you examine it or try to rephrase it in simple language. AI can hallucinate—i.e. make up statements—and this can be obvious or subtle. For example, AI can give correct answers to questions it has generated but give the wrong explanations.

The data that the model is trained on is not necessarily scientifically accurate, so generated text could be incorrect or biased. AI can be prompted to provide references, but these are often not reliable.

AI-generated answers may not model the complete response that aligns with the scope and scale of the syllabus. In class, you will have developed an understanding of the scientific concepts described in the syllabus. In this way, you can check the level of information and accuracy provided in an AI-generated response.

Check with your teacher before using AI in your work.

Acknowledge use of AI using referencing conventions.

Always fact check AI-generated text and references.

Referencing AI sources

You must properly acknowledge the use of AI in your work. Some AI tools provide a URL that will link to generated text. If yours does not, it is a good idea to include the prompt you used and the AI output as an appendix to your work. The following are sample ways to reference AI-generated text (Table 1.8.7).

TABLE 1.8.7 Examples of ways to reference AI-generated text

Referencing style	General format	Example
APA	Author. (Year). Title of software program (Version). Date. URL. Appendix.	OpenAI. (2024). *GPT-4o*. 20 June 2024. URL or 'see Appendix for prompt used and output generated'.
Chicago	Footnote number. AI tool used, Month Day, Year, Creator of tool, URL, Appendix.	1. Text generated using GPT-4o, June 20, 2024, OpenAI, URL or 'see Appendix for prompt used and output generated'.

Prompting the digital assistant

Learning to write effective prompts is essential to get good results from AI. There is no perfect way to write a prompt, but using one of the many frameworks can be useful. Keep the instructions simple—for example:

- Role (Who the chat assistant is being: e.g. policymaker, marketer, consumer)
- Task (What output you would like: e.g. an article, summary, set of questions)
- Format (What it should look like: e.g. bulleted list, table, graph)

For example: I am a government policymaker working on energy strategy. Give me a one-page summary of the pros and cons of producing nuclear power in Australia. Consider cost, climate change, security, the environment and First Nations' perspectives in your answer. Present the summary in bullet points and include accurate references for all data.

If necessary, you can refine the results using further prompts. Note that chat assistants are not predictable, and you can get different results using the same prompt.

MULTIMODAL PRESENTATIONS

Student experiments and research investigations are focused investigations resulting in a conclusion related to the initial question posed. In schools, the process occurs over a number of lessons, but in research science, a project can continue for weeks, months or years. The reporting of the final findings is usually a written report published in a scientific journal, but can also take place at a scientific conference. In the Chemistry syllabus, you are also provided this flexibility in the form of multimodal presentation as an alternative to the written report.

It is important to note that this mode gives you an option for the final presentation of the task only. All criteria and descriptors in the ISMG relating to forming, finding, analysing and interpreting/evaluating need to be met as described in Parts B and C. Multimodal presentations must include at least two modes of delivery at the same time, have a maximum time of 11 minutes and maximum 2000 words. Your two modes are likely to be visual (poster or digital presentation and speech). For average speaking speed, 11 minutes will equate to around 1600–1700 words. Your teacher will need the poster or digital presentation printed and a printed script—they may record your presentation. Another option is to use the audio record function in the presentation software. These aspects of assessment will be identified by the school on their endorsed task(s).

Some considerations regarding the speech are:

- engage and effectively communicate with the audience
- use a clear structure—it is suggested to follow the outline of a written report (see headings provided in Parts B and C)
- interact with your presentation or poster to point out important aspects
- while it is not advisable to speak on a tangent or set up a conversation with the audience, it would be possible to ask the audience if they have any questions
- use a strong confident tone
- bring your own timer to avoid going over time.

Some considerations regarding the visual presentation:

- each slide should have a clear focus with minimal text (6–7 lines per slide, 6–7 words per line). Use minimum 24 font size so that the audience can read
- present a single graph or table per slide. For graph axes or annotations in smaller font, you should read out the information
- use a consistent design or theme.

Some considerations regarding poster:

- use a presentation size large enough to include all your graphs, figures and text
- make the poster 'flow' so the reader clearly follows the investigation from planning to concluding and evaluating
- allow your audience some time before the presentation to view the information and allow them to formulate questions.

Communicating experimental or research findings is an integral part of a scientist's work. Irrespective of the time span of the investigation, there is a sense of achievement when the results are made known, especially when the process requires you to relate to the topic in depth. By choosing a verbal presentation, you can share this journey with the audience.

1.8 Review

SUMMARY

- Scientific reports use scientific language and representations.
- The language of scientific reports is concise, objective and written in the third person.
- The scientific visual representations include tables, charts, graphs and illustrations.
- Visual representations include headings, labels, captions, descriptions, and numbering (if more than one item).
- A science journal is a useful tool for recording detailed information and sources during an investigation.
- Write using your own words to avoid plagiarism.
- Acknowledge sources and any references to the work of others by including a reference list.
- If using AI for scientific research, ensure information is checked against other sources, and acknowledge the AI source to avoid plagiarism.
- A written or multimodal format may be used for your report, but the same syllabus criteria and descriptors apply to both formats.

KEY QUESTIONS

Describe

1 Explain the difference between a bibliography and a reference list.

2 Describe what plagiarism is and indicate why it is unacceptable.

PART B STUDENT EXPERIMENT

The student experiment (IA2) requires students to undertake the full **scientific method**. The QCAA Chemistry General Senior Syllabus 2025 states that this process begins with a practical conducted during class or viewed online. This practical will be modified to conduct your own experiment. It is recommended that during the class practical, you record your observations, queries and thoughts, as well as collect and process data. These notes can be used to develop a research question for the student experiment. This task assesses syllabus objectives and science inquiry skills and relates to student experiment objectives and specifications from the Chemistry syllabus. The student experiment constitutes 20% of the total assessment and may be presented in:

- written form (e.g. scientific report), up to 2000 words or
- multimodal presentation form (at least two modes delivered at the same time), up to 11 minutes.

In the modules that follow, you will find a guide to a scientific method and an outline for producing a report of the student experiment.

INSTRUMENT-SPECIFIC MARKING GUIDE

Student responses are assessed against an instrument-specific marking guide (ISMG). In developing your experiment and planning your response, it is important to always have in mind the assessment objectives, particularly the characteristics that are described in the performance level descriptors.

- The ISMG has four criteria (criterion): forming, finding, analysing, and interpreting and evaluating.
- Criteria have performance levels, against which the qualities of the response are assessed.
- A performance level consists of a performance level descriptor and performance level mark or mark range.
- The performance level descriptor describes the characteristics that are demonstrated by a response at this quality.
- The ISMG criteria and elaborations of each are shown in Table A for the highest performances.

TABLE A Alignment of syllabus criteria, objectives, descriptors and marks with the modules of Part B

Criteria	Assessment objectives	Instrument-specific marking guide (ISMG) – Criteria are demonstrated by:	Marks	Module
Forming	1. Describe ideas and experimental findings about chemical equilibrium systems or oxidation and reduction. 2. Apply understanding of chemical equilibrium systems or oxidation and reduction to modify experimental methodologies and process data. 6. Investigate phenomena associated with chemical equilibrium systems or oxidation and reduction through an experiment.	• a considered rationale for the experiment • justified modifications to the methodology • a specific and relevant research question • a methodology that enables the collection of sufficient and relevant data • appropriate use of genre and referencing conventions	5	1.9 1.8
Finding	1. Describe ideas and experimental findings about chemical equilibrium systems or oxidation and reduction. 6. Investigate phenomena associated with chemical equilibrium systems or oxidation and reduction through an experiment.	• considered management of risks/ethical issues/ environmental issues • collection of sufficient and relevant raw data • fluent and concise use of scientific language and representations	5	1.10 1.8
Analysing	2. Apply understanding of chemical equilibrium systems or oxidation and reduction to modify experimental methodologies and process data. 3. Analyse experimental data about chemical equilibrium systems or oxidation and reduction.	• correct and relevant processing of data • thorough identification of relevant trends/ patterns/relationships • thorough and appropriate identification of the uncertainty and limitations of evidence	5	1.11

Criteria	Assessment objectives	Instrument specific marking guide (ISMG) – Criteria are demonstrated by:	Marks	Module
Interpreting and Evaluating	4. Interpret experimental evidence about chemical equilibrium systems or oxidation and reduction. 5. Evaluate experimental processes and conclusions about chemical equilibrium systems or oxidation and reduction.	• justified conclusion/s linked to the research question • justified discussion of the reliability and validity of the experimental process • suggested improvements and extensions to the experiment that are logically derived from the analysis of evidence	5	1.12
Total			20	

The final report for the student experiment may be organised under the criteria headings in the ISMG: Forming, Finding, Analysing, and Interpreting and Evaluating. However, this is not mandated, and you may elect to organise your report in a different but logical order using alternate headings.

Note that items in the appendix, reference list and in-text references are not included in the word count. The contents of the appendix are not used for determining levels of achievement.

The headings and sub-headings in Table B show one possible structure of a student experiment report (*alternate position of Conclusion section):

TABLE B Possible student experiment structure. Two possible positions for the conclusion

Forming	Rationale
	Research question
	Modifications
Finding	Risk assessment
	Raw data
Analysing	Sample calculations
	Processed data
	Analysis
Interpreting and evaluating	Conclusion*
	Evaluation of experimental process (reliability and validity)
	Improvements and extensions
	Conclusion*
	Reference list/Bibliography
	Appendix

1.9 Forming

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand how to identify and modify an experimental investigation
- be able to research relevant background information that informs the research question
- develop the investigation by forming a research question that includes specific variables
- justify modifications to the original experiment.

RATIONALE

Your student experiment uses a completed class practical or simulation as the basis for further experimentation. This means that the rationale will show an idea flow that begins with an original experimental result and uses scientific reasoning to propose a new and related question (Figure 1.9.1). Often, the same or similar experimental apparatus is used, but the independent and/or dependent variable(s) are altered. Conversely, a new experimental design and equipment is used to investigate the topic.

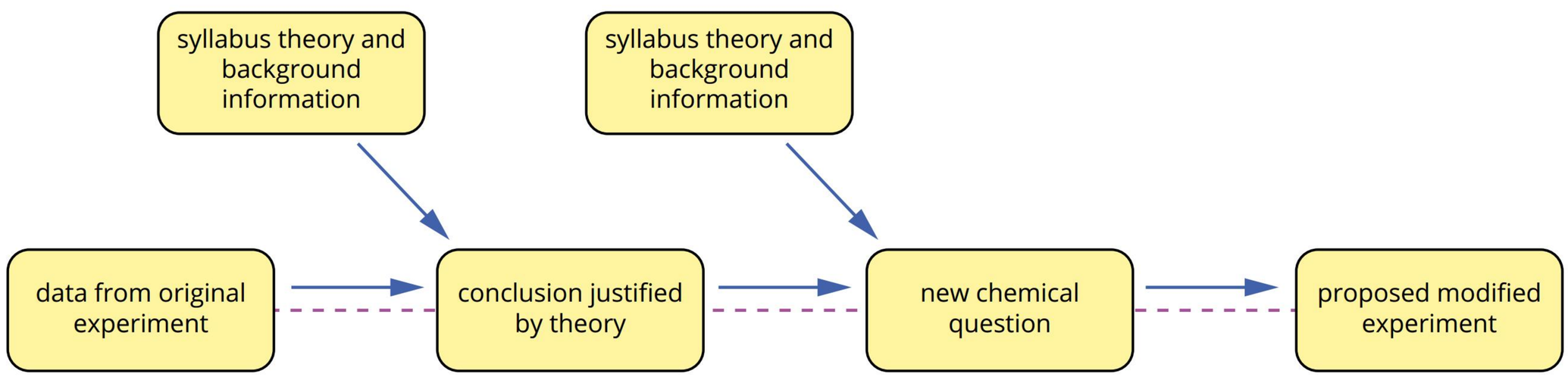


FIGURE 1.9.1 Idea flow for the reasoning process involved for the rationale

A new chemical question is developed from chemical understanding and the result of the original experiment.

Background information

The chemical concepts of both the original experiment and the proposed new experiment need to be described, but it is important to restrict this to the necessary information—a full topic explanation or literature review is not required. Make sure that key syllabus concepts are included using relevant chemical equations, structures and diagrams. Background concepts from scientific literature need to be referenced using in-text referencing. You will need to read widely, but limit your use of chemical concepts to the scope of the syllabus. If your original experiment and proposed new experiment cannot be explained using syllabus concepts from the appropriate unit, change your experimental focus. A summative student experiment needs to be based on science understanding from Units 3 and 4. Your explanation of background information should demonstrate understanding and knowledge of the direct, and possibly indirect, relationship between the independent and dependent variables and controlled or measured variables.

The syllabus states that the task requires students to 'research relevant background scientific information to inform the modification of the research question and methodology'.

Here we see:

- 'relevant', which means background scientific information related to the syllabus as well as relevant to your experiment
- 'inform', which means you have used science concepts to identify a new experiment
- 'modification', which means the new experiment is related to the first one, but the variable(s) and/or method are modified.

Group planning

Parts of the experiment can be completed with your group. For instance, it is appropriate to discuss the findings of the original experiment to be clear about the relationship shown in the data. Also, the group could discuss changes to the method or the dependent and independent variables that may be appropriate. You will collect data together; however, the rest of the investigation including analysis, evaluation and report writing is an individual task.

Discuss what you have already learnt in class about the topic and possible or expected relationships that which could be investigated (Figure 1.9.2). Develop a specific research question stating the proposed dependent and independent variables. This relationship will be the focus of your research question. In addition, you may propose a refinement of equipment or methodology, which will need to be discussed and clarified with your teacher. Check that your school laboratory has the resources for you to perform the experiment or investigate the topic. Choose a topic that can provide clear measurable data that show how variable y depends on variable x.

Consider the following when developing the modified experiment:

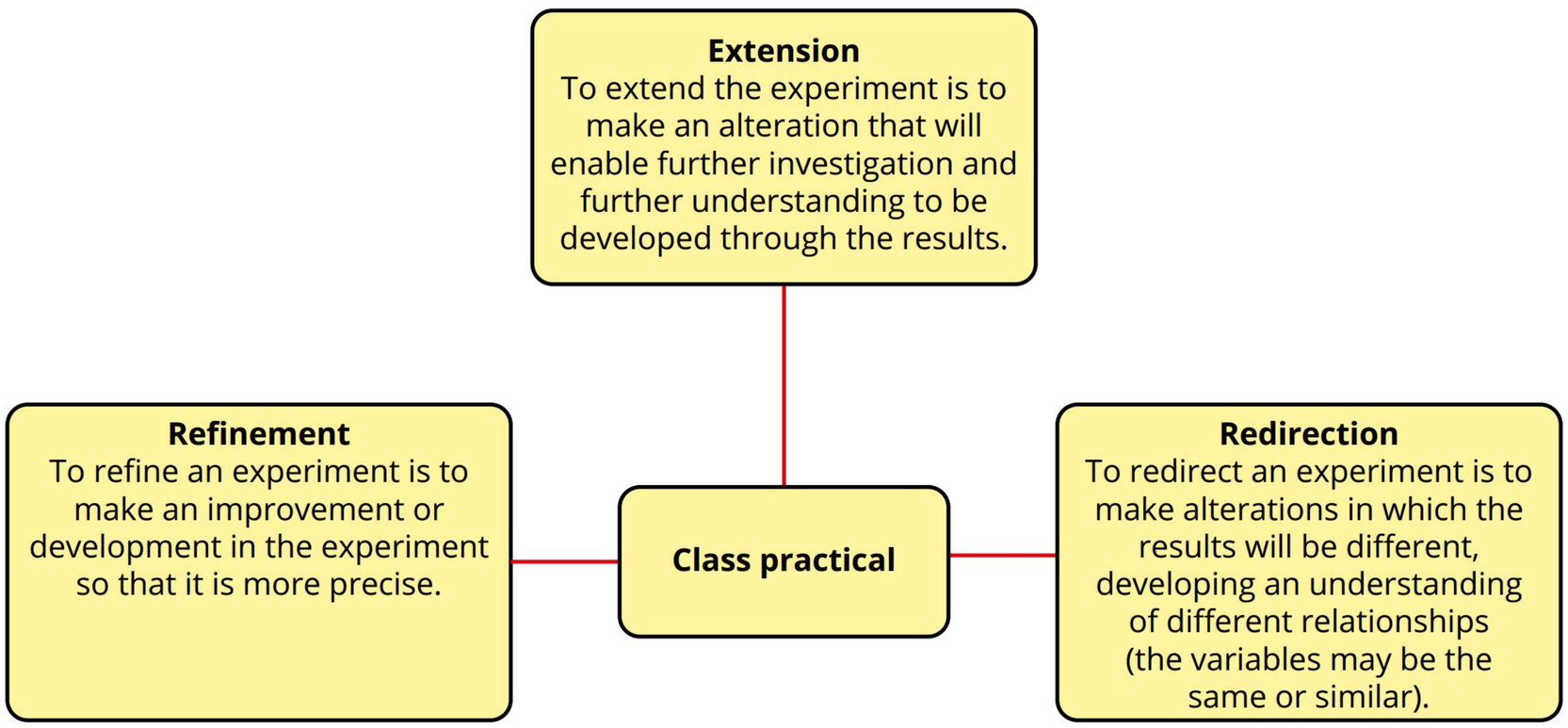


FIGURE 1.9.2 Changes that can be made to a practical to develop the student experiment

Table 1.9.1 shows examples of changing an original experiment into a topic of interest for a student experiment.

TABLE 1.9.1 Examples of modifying a practical into a student experiment

Original experiment	Possible modified experiments
Conduct a calorimetry experiment to measure the enthalpy of the combustion of hexanol.	Does using less water in the calorimeter increase the accuracy in determination of the combustion of hexanol?
	Is the accuracy of the molar heat of combustion of hexanol improved by using multiple trials?
	Can the experimental method be used to determine molar heat of combustion of other alcohols?
	Can the apparatus be altered to limit heat loss and increase accuracy of enthalpy of combustion of hexanol?

Defining the variables and data collection

The factors that can change during your experiment or investigation are called variables. An experiment or investigation determines the relationship between variables by measuring the results. There are four categories of variables (Figure 1.9.3). You should have only one **independent variable**. Otherwise, you could not be sure which independent variable was responsible for changes in the **dependent variable** (the results). It is best to think of a single variable (independent variable) that may influence the measured outcome (dependent variable). Use clear dependent and independent variables, include values for concentrations, and be specific about number of trials. The more variables that are altered (including **measured variables** and **controlled variables**), the more complex the task becomes.

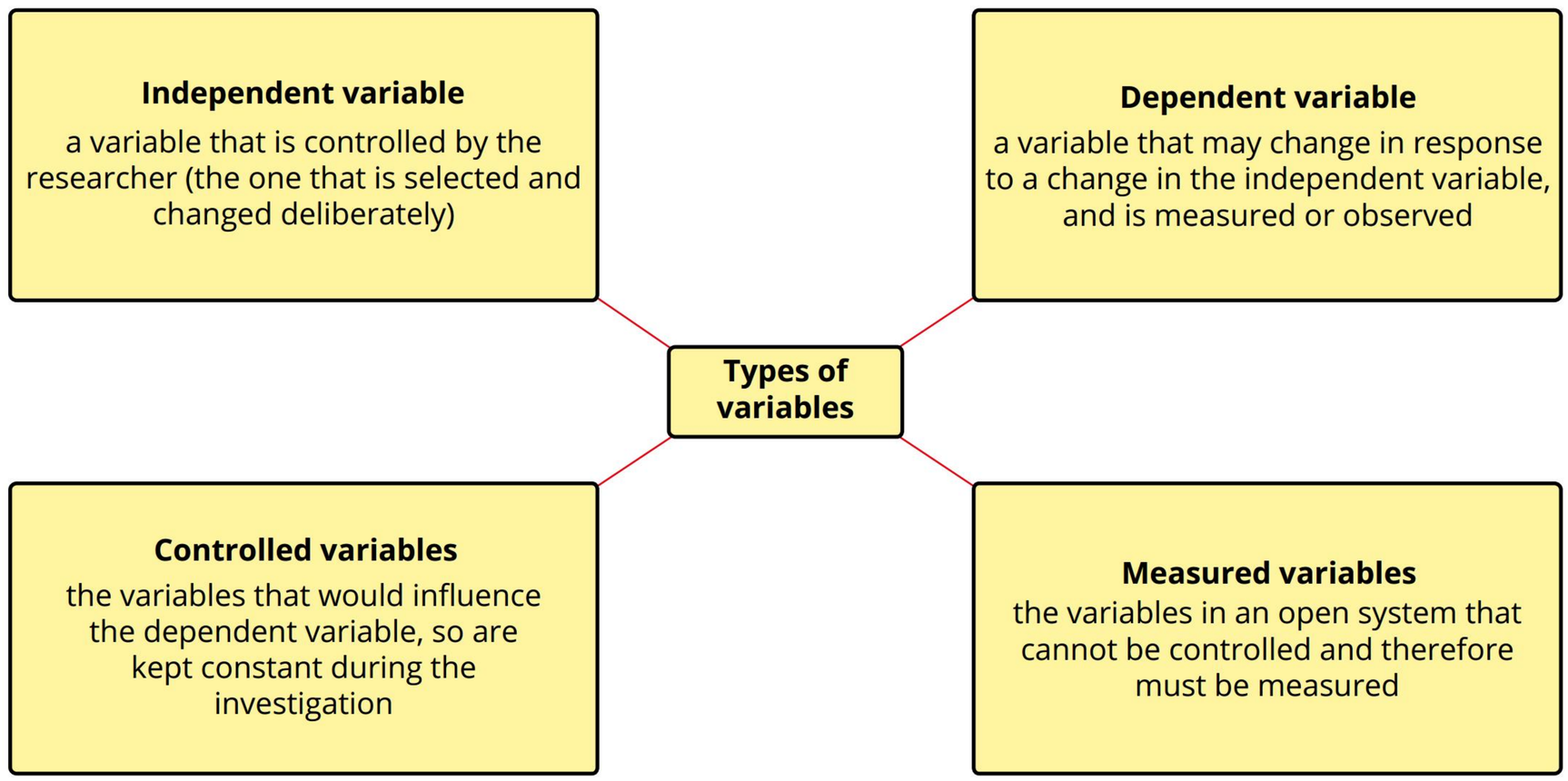


FIGURE 1.9.3 The four types of variables in experiments

To ensure an investigation is **valid**, it should be designed so that only one variable is being changed at a time. The remaining variables must remain constant so that meaningful conclusions can be drawn about the relationship between variables. In junior science, we learn "Change one thing, measure one thing, keep everything else the same". In your Rationale and Research Question discussions with your group and teacher, you will consider the:

- independent variable (the thing that is changed)
- dependent (measured) variable
- controlled variables (parts of the equipment, method and conditions that are constant)
- appropriate raw data that will be collected (quantitative versus qualitative), and how each will be measured, collected or controlled.

Data can either be qualitative or quantitative. **Qualitative data** is descriptive and unmeasurable and uses descriptions or adjectives to record observations. It cannot be statistically analysed. **Quantitative data** is empirically measurable and uses instruments to record observations as numbers with units.

Qualitative and quantitative data have further subsets in each category (Figure 1.9.4).

Qualitative data can be observed but not measured.
It can only be sorted into groups or categories such as flower colour or leaf shape.

Nominal data
Variables are categorical variables in which the order is not important.
Example 1: the type of metal, type of apparatus
Example 2: genotypes—AA, Aa or aa

Ordinal data
Variables are categorical variables in which order is important and groups have an obvious ranking or level.
Example 1: the level of brightness of light globes
Example 2: perceived exertion from 1 to 10 in an aerobic endurance test

Quantitative data can be measured.
Height, mass, volume, temperature, pH and time are all examples of quantitative data.

Discrete data
Variables consist of only integer numerical values, not fractions.
Example 1: the number of springs connected together
Example 2: the energy levels in atoms

Continuous data
Variables allow for any numerical value within a given range.
Example 1: the measurement of height, temperature, volume, mass and pH
Example 2: time for a cart to slide down a ramp

FIGURE 1.9.4 Quantitative and qualitative variables

Measurement of temperature requires an instrument and provides quantitative data, whereas sensing the production of heat by touch provides qualitative data (Figure 1.9.5).

FIGURE 1.9.5 (a) A liquid thermometer for measuring water temperature. (b) Feeling heat radiating from a heater is an example of qualitative data as it is based on personal observation. Qualitative data cannot be statistically analysed.

Depending on the experiment, it may be appropriate to record the qualitative observation (e.g. colour change or precipitate formation during a chemical reaction), or perhaps measure the quantitative results (e.g. voltage of a Galvanic cell).

Sourcing appropriate equipment and materials

You will need to decide on the materials, technology and instrumentation that will be used to carry out your experiment or investigation. It is important to find the right balance between items that are easily accessible and those that will obtain accurate and precise results. The precision of the chosen instrumentation affects the level of measurement uncertainty and is recorded as a ± value in the raw data table.

Sample size

Because a single measurement or experimental result could be affected by errors, **replication** of samples within an experiment and **repeat trials** are key components of reliability. A larger sample size will improve:

- the representation of the phenomenon
- identification of natural variation, errors and uncertainty
- the results by offering more evidence to support the experimental results
- aids with repeatability and therefore reliability.

Consider the practicalities of timing and validity of data in determining the number of trials and the number of independent variables tested. Given that 10 hours are allocated to planning the experiment, performing the experiment and writing the report, consider that about 15 trials may be sufficient. At least 3 trials per independent variable are generally required. If you are expecting a linear relationship, 3 values of the independent variable may be sufficient, but if the expected relationship is logarithmic, 5 or more data points would be required.

Writing a research question

When you have decided on a dependent variable, independent variable, controlled variable(s) and method of testing, you are ready to write your research question.

A research question directs and describes the scientific inquiry activity. Its purpose is to focus the student experiment, inform the direction of the research and guide all stages of inquiry, analysis, interpretation and evaluation.

The question determines the experiment and the experiment is testing the question. A research question should:

- be specific and relevant to the class experiment
- clearly identify the subject matter of the experiment
- specify the scope or conditions of the inquiry
- aim to find trends or patterns of relationships between two variables.

A research question should state the independent and dependent variables. It should ask if the independent variable will affect the dependent variable. The research question must specifically outline variables in a way that is measurable; this also allows the research question to be answered.

Look at this example below.

independent variable

'How does changing the concentration of the HCl affect the rate of the reaction between HCl and Mg as shown by reaction time at completion when temperature and mass of Mg are constant?'

dependent variable

A well-constructed research question should have the following characteristics.

- It should include measurable variables—the independent variable and the dependent variable.
- It should have a guiding word, such as *how*, *what* or *will*.
- It should be phrased so that a definitive answer can be developed.
- It should state key (not all) controlled variables or conditions.
- It can state a proposed relationship.

Table 1.9.2 gives examples of constructed research questions.

TABLE 1.9.2 Structuring a research question

Guiding word(s)	Example research questions
will	Will increasing the reaction temperature (10°C, 20°C, 30°C) increase the rate of the reaction between 2 g zinc pieces and 20 mL 0.5 M hydrochloric acid?
how	How does changing the concentration of the cathode solution, $Cu(NO_3)_2$, from 0.1 M to 2.0 M, while keeping the anode, $Zn(NO_3)_2$, concentration constant (0.1 M), affect voltage produced by a galvanic cell?
can	Can an increase in particle size decrease the rate at which 25 g solid sugar dissolves in 100 mL 20°C water?
do/does	Does acid concentration (0.1 M, 0.3 M, 0.6 M) affect conductivity of H_2SO_4 and HCl solutions at 25°C?

Evaluating your research question

Once a research question has been developed, stop to evaluate it before progressing. Follow the prompts in the chart below (Figure 1.9.6) to refine and improve it.

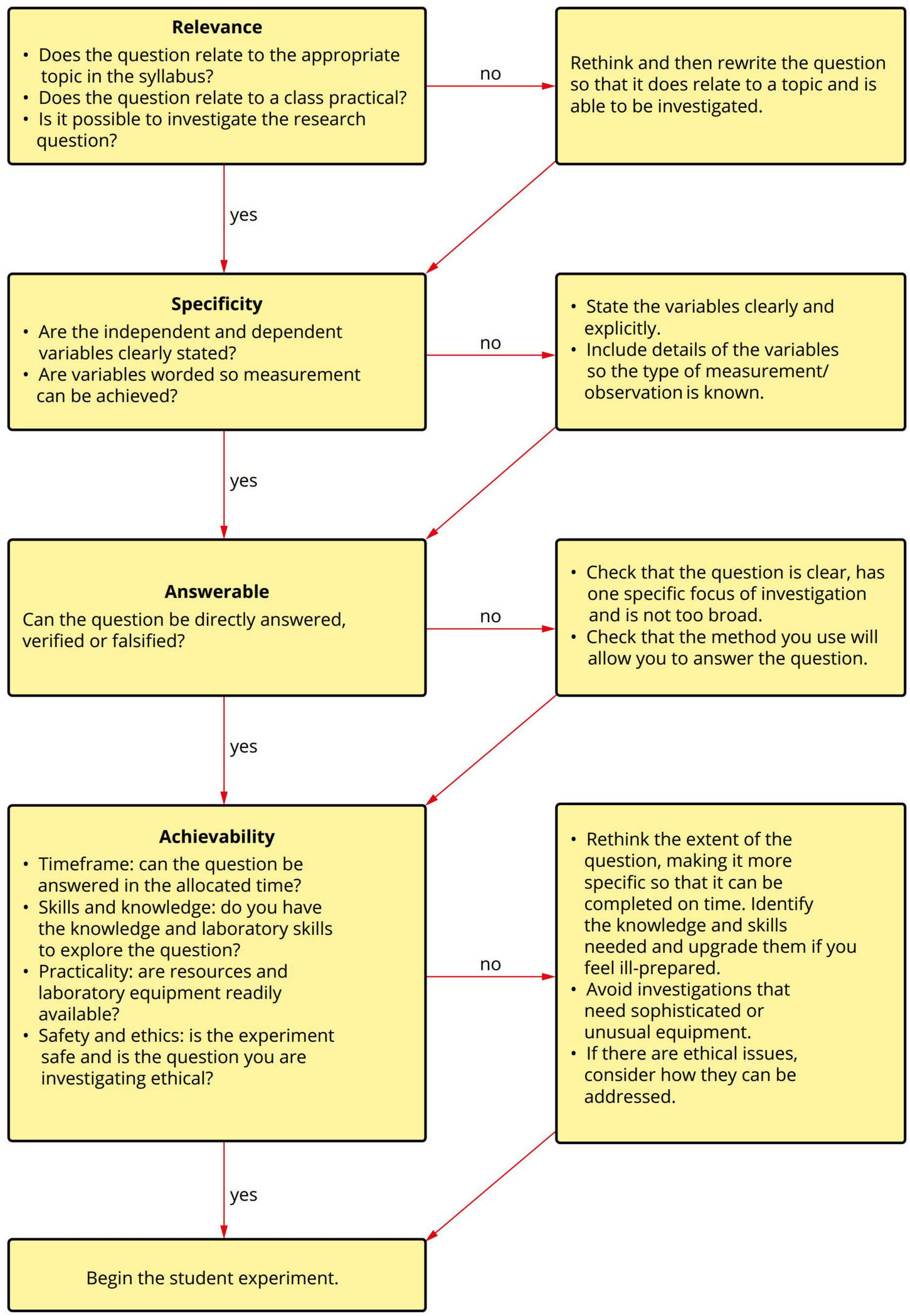


FIGURE 1.9.6 Steps to refine and improve the research question.

A research question proposes a question about the relationship between the dependent and independent variables of the investigation. It is a required component of the student experiment.

A hypothesis defines the expected link between the dependent and independent variables and supports the research question, but is not an assessed component of the ISMG.

A hypothesis is a statement that proposes a relationship between variables and an expected result of the experiment—it is based on some level of understanding. Having completed extensive background research (Rationale), you will have the means and understanding to state the expected results in the form of a hypothesis.

The student experiment does not require a hypothesis and it may not always be appropriate or beneficial. Because the hypothesis proposes a specific relationship between the independent and dependent variables, the hypothesis can either be supported or refuted by the results. Figure 1.9.7 shows key components of a hypothesis.

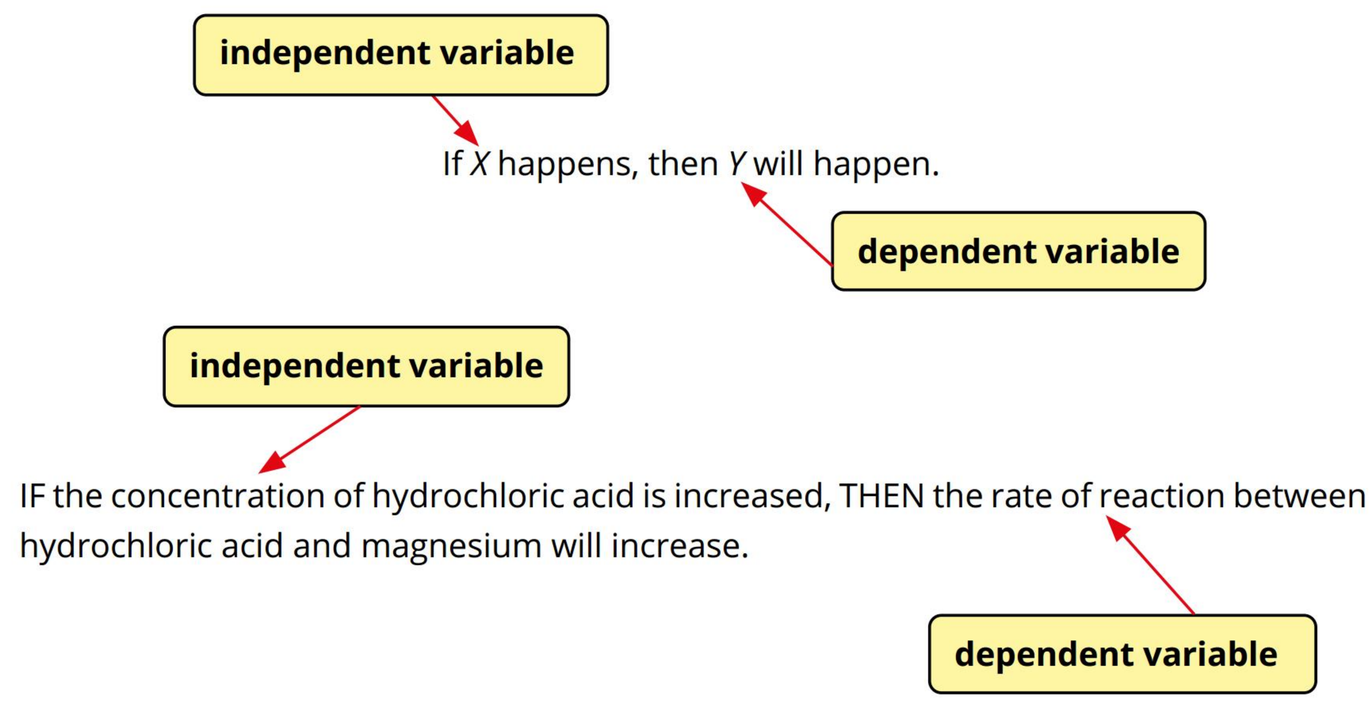


FIGURE 1.9.7 The key cognitions in the development of the research question—in terms of the dependent and independent variables

Table 1.9.3 shows research questions and the associated relationship between the dependent and independent variables.

TABLE 1.9.3 Research question examples

Relationship between the dependent and independent variables	Research question
As the temperature of the gas increases, the volume of the gas will increase.	How does the volume of air in a syringe change as the temperature of the air is increased from 20 to 80°C?
The rate of reaction will increase and time for production of 25 mL gas will decrease as the temperature of the reaction mixture increases.	Does the time taken for the production of 25 mL of hydrogen gas decrease as the temperature of the solution of 50 mL 0.5 M hydrochloric acid and 5 g zinc is increased?
The accuracy of the measured molar enthalpy of combustion of ethanol will be increased by performing multiple calorimetry experiments.	Does burning different masses of ethanol (2 g, 4 g, 6 g) in multiple calorimetry experiments improve the accuracy of the determination of the molar heat of combustion?

Justified modifications to the methodology

The previous section shows the complexity of the Forming (planning) part of the student experiment. You (and your group and teacher) will have decided on key aspects of the modified experiment—independent, dependent and controlled variables, identified a procedure and equipment for use and written a research question. It is necessary to document each modification to the original experiment in your report and justify each proposed modification.

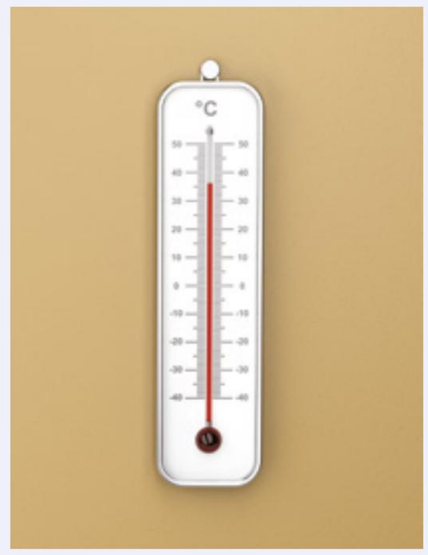
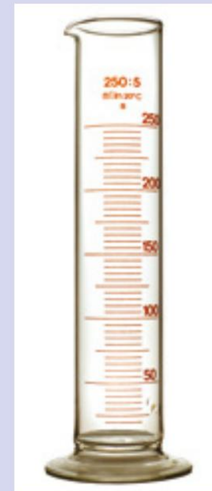
The methodology of your experiment is a specific step-by-step procedure that your teacher will require you to prepare prior to the experiment. However, this detail is generally not required in the report. In the modifications section, write an overview of the original method (use an in-text reference) in paragraph form and provide a written or tabulated description of the modifications proposed. Include specific details about instruments, chemicals (with concentrations), techniques employed and number of trials. Each modification is justified by stating the type of change ('refine', redirect' or 'extend') and how it will improve the investigation. If possible, link each modification to both random and systematic errors. An example is shown in Table 1.9.4.

TABLE 1.9.4 Examples of changes to the original experiment with justification

Modification	Type of change	Justification
Replacing the filter paper salt bridge with an agar salt bridge.	Refinement	Provides consistent circuit connection and ion flow and reduces random error.
Collection of more data—five trials for each concentration rather than one.	Refinement	Provides an average and uncertainty of evidence.
Measuring the cell potential difference of one Zn/Zn^{+2}| Cu/Cu^{+2} galvanic cell.	Redirection	Investigates the effect of concentration change on the cell potential of one galvanic cell.
Use a range of concentrations of copper nitrate solutions, consisting of 0.1 M, 0.5 M, 1 M, 1.5 M, 2 M.	Extension	Provides an understanding of how the concentration of a substance can affect the cell potential of the galvanic cell.
Pasco digital Bluetooth voltmeter rather than a Dick Smith analog voltmeter.	Refinement	Provides more reliable readings of voltage and reduces possible systematic error.

One way to modify an original experiment is to improve the precision of the laboratory equipment. With higher-precision instruments, there is less chance of error and lower uncertainty in the measurement. Table 1.9.5 demonstrates the benefits of greater-precision instruments through lower measurement uncertainty.

TABLE 1.9.5 The difference in measurement uncertainty between instruments: (a) a glass thermometer with a precision of ±2.5°C; (b) a measuring beaker with a precision of ±5 mL; (c) an in-ear digital thermometer with a precision of ±0.1°C; and (d) a measuring cylinder with a precision of ±2.5 mL

Lower-precision instruments	Higher-precision instruments
a 	c
b	d 

PUTTING IT ALL TOGETHER

The sample experiment report shown below follows the ISMG criteria. While this example may be used as a reference tool, note that IA2 must relate to Unit 3 subject matter.

An investigation into the effect of concentration on the temperature of crystallisation of potassium chloride

Rationale

Water is an effective solvent because it dissolves polar covalent and ionic substances. Ionic compounds dissolve due to ion–dipole attraction. Oxygen's electronegativity (3.5) and hydrogen's electronegativity (2.2) create a dipole in water, attracting ions. This process is shown in Figure 1 with potassium chloride (KCl). The solubility of a substance is dependent on these interactions occurring, but it is also affected by the strength of the ionic lattice itself. A stronger lattice causes less dissolving, but strong interactions between solute and solvent cause more dissolving. Heating the solvent (water) increases solute dissolving due to the increase in kinetic energy of all particles (solvent and solute), which increases collisions as well as increase the movement of bonded atoms (Holmes et al., 2019).

Cooling a saturated solution leads to precipitation (BBC, 2022). In the original experiment, the relationship between solubility (maximum dissolving solute amount) of KNO_3 and temperature was investigated by cooling a KNO_3 solution of known concentration, observing crystallisation and constructing a solubility curve—it was shown that as temperature increases, solubility increased. At 25°C, maximum dissolving amount of KNO_3 was 32 g per 100 g water, and at 40°C, 60 g was the maximum amount dissolved in 100 g water.

In the modified experiment, the precipitation of the ionic compound potassium chloride (KCl) will be investigated instead of potassium nitrate (KNO_3). The bonds of KCl form a lattice structure (potassium cations (K^+) and chlorine anions (Cl^-), as shown in Figure 2). The strength of the lattice is based on the electrostatic forces between cations and anions (Ashenhurst, 2021). The current experiment seeks to determine the change in the solubility of KCl with temperature by constructing a solubility curve. Also, by investigating the dissolving of an ionic compound that has the same cation as the original experiment but a different anion, the current experiment will show if the trend identified in the original experiment holds true for another ionic compound.

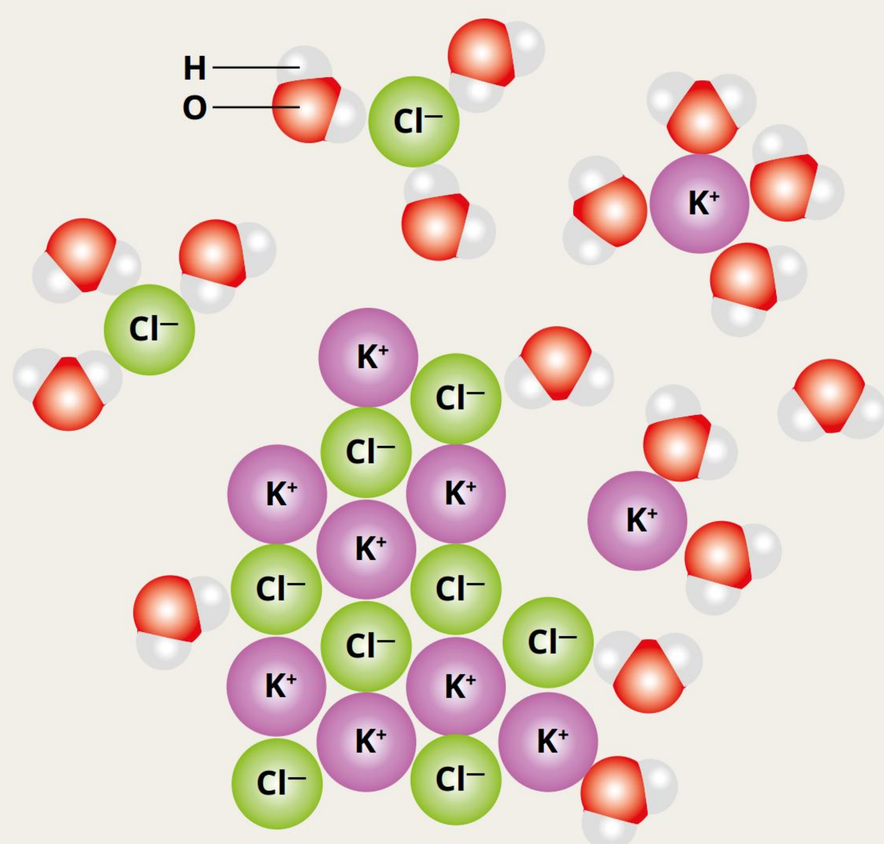


FIGURE 1 H_2O forming dipole interactions with KCl

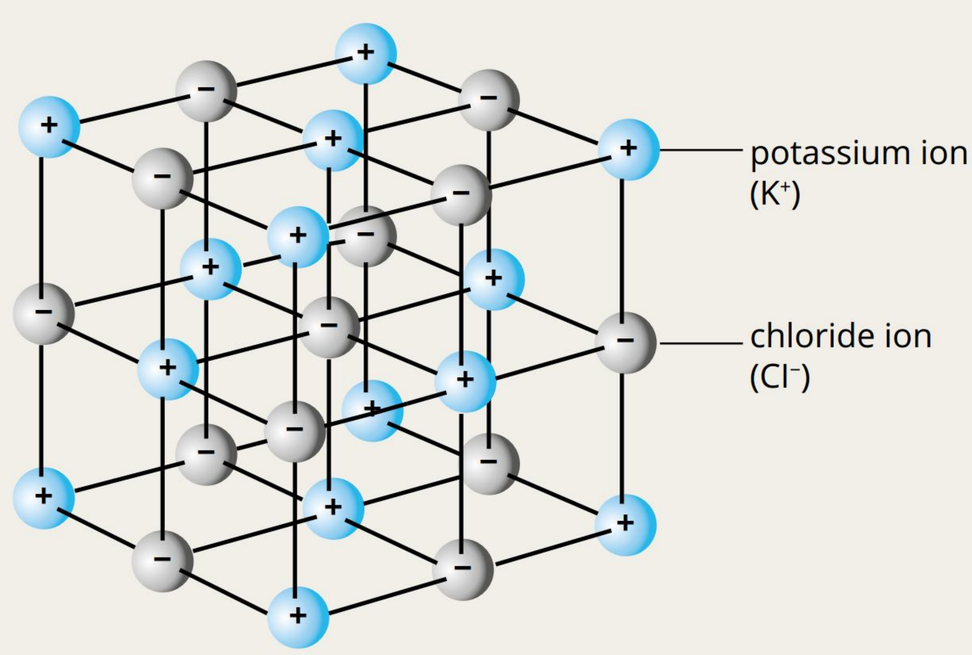


FIGURE 2 Lattice structure of KCl

Research question

How does increasing the concentration of KCl (36 g/100 mL, 40 g/100 mL, 44 g/100 mL and 48 g/100 mL) affect the temperature at which crystallisation occurs in a 5 mL solution?

Original experiment

The initial experiment dissolved the ionic substance, KNO_3, in water at concentrations between 40 g/100 mL and 120 g/100 mL by heating with a Bunsen burner. After dissolution, the test tubes were allowed to cool until crystallization occurred, and the solution's temperature was recorded (Figure 3). The modifications made to this experiment are shown in Table 1.

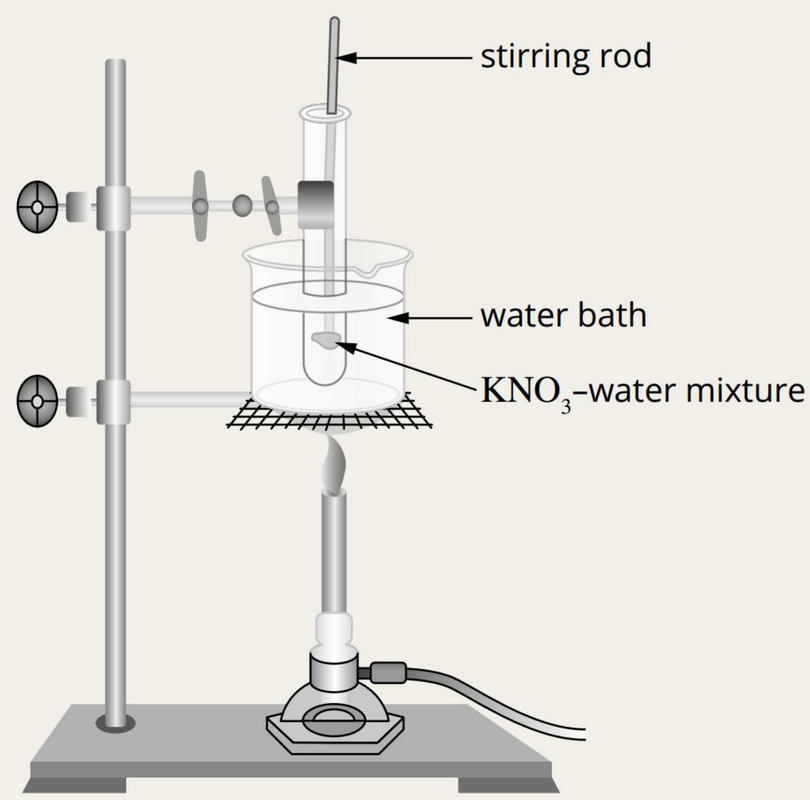


FIGURE 3 Original experiment set-up (Huddart, 2019)

TABLE 1 Modifications to the original methodology

Modification	Justification
The experiment was **refined** by increasing the sample size from one trial to five.	This enables the collection of sufficient raw data so that an average temperature is calculated. Conducting more trials enhances experiment accuracy and reliability by identifying and eliminating anomalies, and identifying the trend.
The ionic compound was **changed** from potassium nitrate to potassium chloride.	Changing the solute allows for a greater understanding of solubility trends of potassium-based ionic compounds.
The Bunsen burner with beaker of water was **refined** to a water bath heated by a hot plate.	Using a heated water bath rather than a Bunsen burner allows for greater accuracy as the temperature stays consistent and is controlled.
An additional concentration was added, which **refines** the experiment. 36 g/100 mL, 40 g/100 mL, 44 g/100 mL and 48 g/100 mL	Testing four concentrations instead of three allows for greater confidence in the observed trend.
Expected values are obtained from research and compared to experimental data.	By comparing to expected values, the accuracy and validity of the experiment can be assessed.

FIGURE 4 Experimental set-up—electronic balance, electronic water bath, test tube, rack and funnel, spatula, KCl powder, thermometer

1.10 Finding

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- conduct a risk assessment
- undertake an experiment encompassing sufficient and relevant data
- collect and present data.

RISK ASSESSMENT

When planning for an experiment, it is important for your safety and the safety of others to consider the potential risks. Risks are potential negative outcomes from carrying out an activity. Everything we do has some risk involved. **Risk assessments** are performed to identify, assess and control risks. A risk assessment should be performed for any situation, whether in the laboratory or out in the field, that could cause harm to people or animals.

The first step in the risk assessment process is to assess all risks in the environment in which the experiment or fieldwork will be carried out. This is the inherent risk. The second step is to identify control measures that will reduce the level of risk to low risk. For example, glass equipment in the laboratory is a hazard as it can cause injury if it breaks. Injury is a negative outcome and so it is a risk. A control measure to reduce this risk is handling the glass equipment carefully.

Your report should outline risks, include values, including detail such as the chemical names and concentration values, and explain how the risks will be accounted for (managed). While the key consideration is for the personal safety of the people in the laboratory, you need to consider and include a statement about potential effects on the environment. The ethics of the investigation are also considered and managed. Ethical and environmental considerations must be mentioned even if there is no risk.

Your risk assessment will have three sections:

- hazard—the name of the item or activity that could cause risk
- risk—the possible negative outcome that could occur
- control measures—the practices or processes recommended to avoid the risk.

Often, the original experiment will have used similar equipment and so information from its risk assessment can be used. Check with your teacher regarding new equipment that you are planning to use.

To identify risks, think about the following:

- laboratory rules of the school; for example, procedures for correct behaviour in a laboratory and procedures for equipment use
- the activity that you will be carrying out, including physical issues such as lifting heavy objects, and how you will use any equipment (such as glassware) or handle chemicals, including sources of heat and electricity
- the facilities of the laboratory. These include emergency equipment on site, ventilation of the laboratory and facilities such as a fume hood
- the chemical codes and Safety Data Sheet (SDS) for chemicals in use. Also, consider the concentrations of chemicals and the hazards associated with the products of chemical reactions
- what protective clothing you should wear (e.g. lab coat and goggles).

Chemical codes

The chemicals in the school laboratory or in a hardware shop have a warning symbol on the label. These symbols are a chemical code indicating the nature of the contents (Table 1.10.1). In 2017, the Globally Harmonised System of Classification and Labelling of Chemicals (GHS) was introduced in Australia for use in workplaces, including school laboratories.

TABLE 1.10.1 GHS pictograms used as warning symbols on chemical labels

GHS pictogram	Use	GHS pictogram	Use	GHS pictogram	Use
	flammable liquids, solids and gases; including self-heating and self-igniting substances		oxidising liquids, solids and gases, may cause or intensify fire		explosion, blast or projection hazard
	corrosive chemicals; may cause severe skin and eye damage and may be corrosive to metals		gases under pressure		fatal or toxic if swallowed, inhaled or in contact with skin
	low-level toxicity; this includes respiratory, skin and eye irritation, skin sensitisers and chemicals harmful if swallowed, inhaled or in contact with skin		hazardous to aquatic life and the environment		chronic health hazards; this includes aspiratory and respiratory hazards, carcinogenicity, mutagenicity and reproductive toxicity

Safety Data Sheets

Each chemical substance has an accompanying document called a **Safety Data Sheet (SDS)** (Figure 1.10.1). An SDS contains important safety and first-aid information about each chemical you commonly use in the laboratory. The SDS provides employers, workers and health and safety representatives with the necessary information to safely manage the risk of hazardous substance exposure.

1. IDENTIFICATION OF THE MATERIAL AND SUPPLIER

Product identifier

Product Name HYDROCHLORIC ACID - 20% OR GREATER

Supplier
Edwards & Tubbs Operations Pty Ltd
ABN: 51 444 444 444
13 Royston Vasey Street
Melbourne 3000
Australia

Emergency telephone number **1900 654 321 (ALL HOURS)**

2. HAZARDS IDENTIFICATION

GHS Classification

Classified as dangerous goods in accordance with the Australian Code for the Transport of Dangerous Goods by Road and Rail (ADG).

Classified as a hazardous chemical in accordance with the criteria of Safe Work Australia - Globally Harmonized System (GHS).

Corrosive to metals	Category 1
Skin corrosion/irritation	Category 1 Sub-category B
Serious eye damage/eye irritation	Category 1
Specific target organ toxicity (single exposure)	Category 3

SIGNAL WORD: Danger

Hazard statements
H290 - May be corrosive to metals
H314 - Causes severe skin burns and eye damage
H335 - May cause respiratory irritation

Precautionary Statements - Prevention
Keep only in original container
Do not breathe fumes, gas, mist, vapours, spray
Wash face, hands and any exposed skin thoroughly after handling
Use only outdoors or in a well-ventilated area
Wear protective gloves / protective clothing / eye protection / face protection

FIGURE 1.10.1 Extracts of a Safety Data Sheet (SDS) for concentrated hydrochloric acid. The SDS alerts the reader to any potential hazards when using a substance, including appropriate measures to reduce risk of harm.

All schools store SDS and chemical code information for materials in use in laboratories, and these must be consulted when planning investigations. Online platforms such as RiskAssess allow quick access to these data bases for a planned experiment. In these types of software programs, the potential hazards for each aspect of the experiment are provided when proposed equipment and materials are listed. Handling procedures are also suggested.

It is important to note that to address the syllabus requirement to show 'considered management of risk', you need to do more than download a data sheet or risk assessment. The syllabus specification requires you to 'conduct a risk assessment and account for risks in the methodology'. This means that, as described above, the three factors of (i) risk, (ii) possible negative outcome and (iii) prevention need to be aligned and clearly presented in the report. This can be done by writing a paragraph or preparing a table (Table 1.10.2). The supporting data sheets or risk assessments should be placed in the Appendix, with key facts used in your report.

TABLE 1.10.2 Sample risk assessment table showing hazards, risks and control measures to reduce the risks

Risk assessment		
Hazard	**Risk**	**Control measures**
glass equipment	breakage of glass	handle cautiously
		stay aware of your surroundings
		listen to teachers' commands
1 M copper sulfate	skin irritation	gloves
1 M potassium nitrate	eye irritation	goggles
1 M zinc nitrate	inhalation: light headedness, respiratory irritation	face mask; handle powder gently
zinc metal	cuts	handle cautiously
copper metal	skin irritation	gloves

Risk controls

The hierarchy of risk controls is shown in Figure 1.10.2. It is organised from the most effective to least effective. The most commonly used risk control measure that addresses the majority of risks is personal protective equipment. The least common but most protective control measure is eliminating the risk from the scientific investigation.

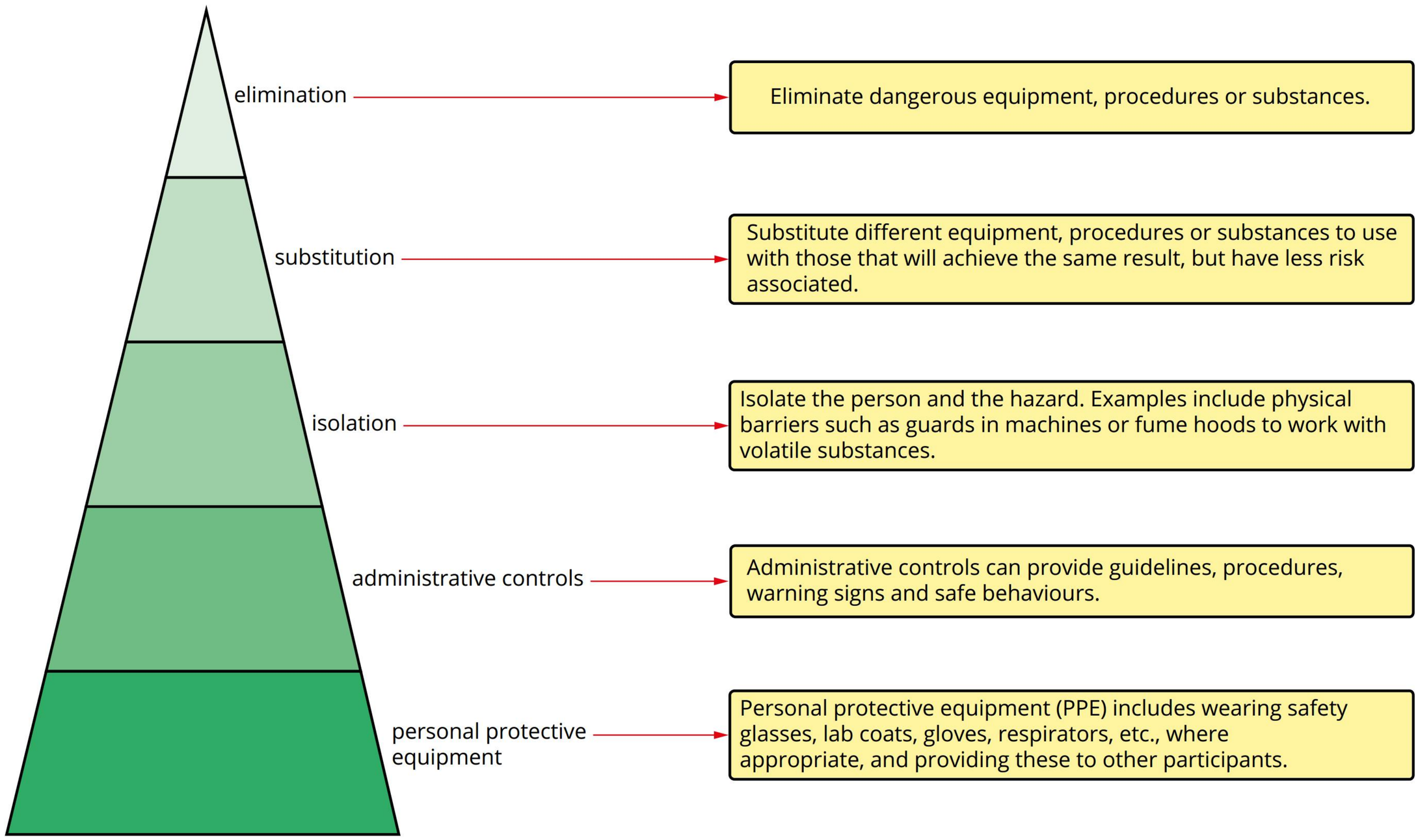


FIGURE 1.10.2 The hierarchy for risk control is shown in this pyramid, marked from bottom to top in order of increasing importance.

Personal protective equipment

Everyone who works in a laboratory wears items that help keep them safe, such as those shown in Figure 1.10.3. These items are called **personal protective equipment (PPE)** and include:

- safety glasses
- shoes with covered tops
- disposable gloves when handling certain chemicals
- a disposable apron or a lab coat if there is a risk of damage to clothing
- hairnet or tied-back when using a Bunsen burner.

FIGURE 1.10.3 Examples of PPE shown are protective eyewear, lab coats and gloves.

Environmental and ethical considerations

When planning an investigation, identify all possible environmental and ethical considerations and evaluate mitigation of issues. Reactants and products of chemical reactions are often toxic to aquatic organisms and, because our wastewater will eventually re-enter the natural environment, many common laboratory solutions (for example, metal sulfates and metal nitrates) must be collected for special disposal rather than tipped into a sink.

Ethics is a set of moral principles by which your actions can be judged as right or wrong. Scientists have to obtain approval from an ethics committee and follow ethical guidelines relating to animals and humans. In reality, school chemistry investigations generally have minor ethical issues, if any. However, consider if during the experiment, one party or group benefits over another, or are there real-world connotations of the investigation not accepting the rights of a community group.

COLLECTION OF SUFFICIENT AND RELEVANT RAW DATA

Enough data need to be collected to substantiate whether or not a relationship exists between the dependent and independent variables. For the data to be relevant, the investigation must collect values for the independent and dependent variables as described in the Research Question. For the data to be *sufficient* means to have appropriate sample size in terms of an appropriate number of replicate trials and an appropriate number of variations of the independent variable. Sample size will affect the accuracy of the data, the uncertainty within the data collected and the ability to interpret the data. In general, a minimum of five data points and three measurements per data point (three trials), or three data points with five measurements per data point (five trials) are needed. This provides a sample size consistent with sufficient and relevant data. Consider your expected trend. If you are expecting a logarithmic or other non-linear trend, you will need at least four or five data points—three would not clearly show the trend. Table 1.10.3 outlines examples of sample size and their effect on the results of an experiment.

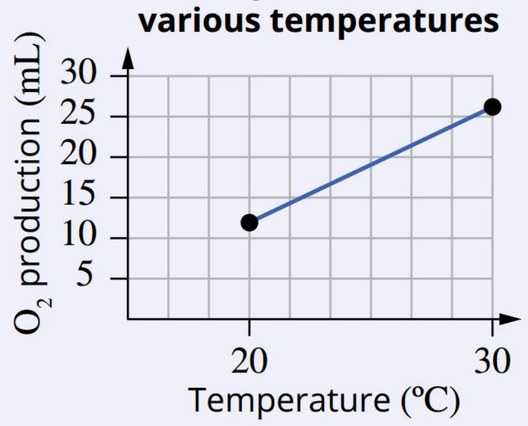
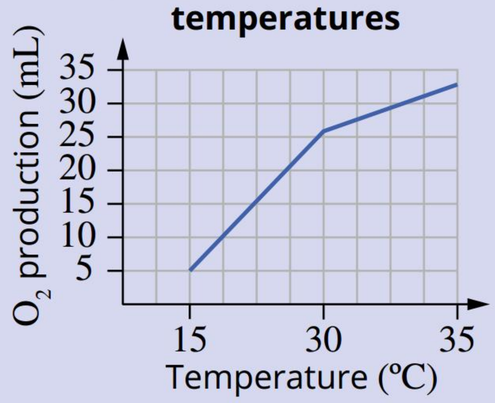
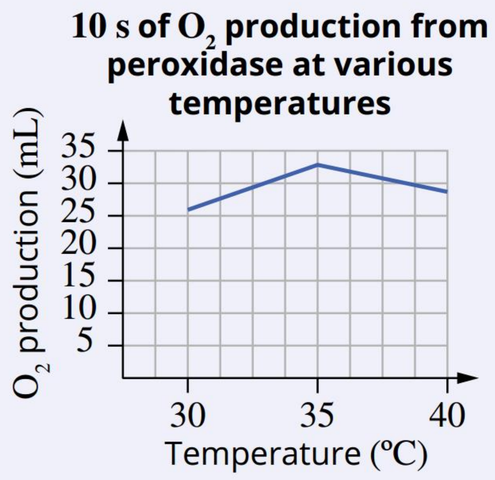
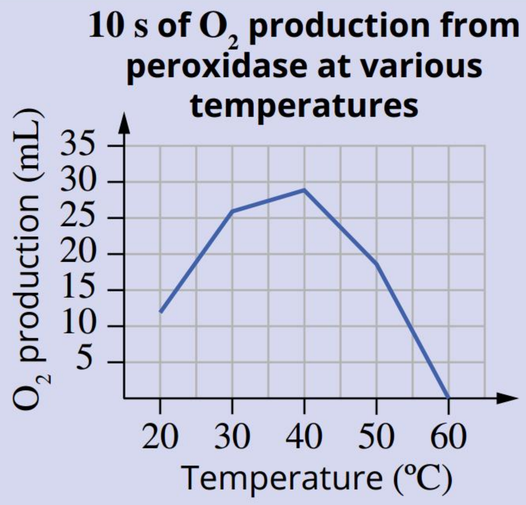
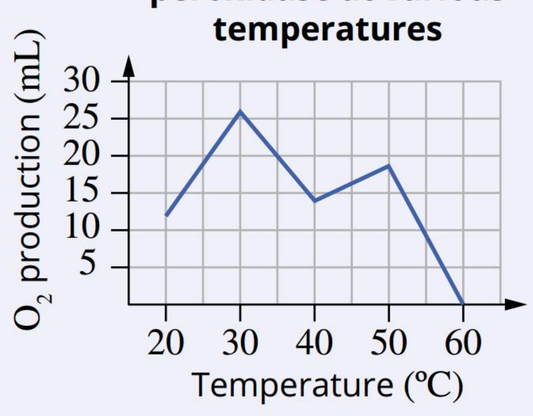
Having determined your sample size, check with your teacher that your protocol and schedule (methodology) are appropriate. You need to be able to perform your experiment independently, in the time available in the school laboratory, and with minimal support from your teachers and school laboratory staff.

It is common for experimentation and testing not to go according to plan even if comprehensive background research has been undertaken. Refinements such as reducing or increasing the sample size may be necessary due to timing issues, change to instrumentation or resource limitation.

If the expected data is not obtained, do not worry. Sometimes, a different point of view, such as from a fellow student or a teacher, is all that is needed to find a solution. As long as the data can be critically and objectively evaluated (limitations of the investigation are identified) in your report, the work is worthwhile. Unexpected data provides students with an opportunity to add depth to their experimental report by critically evaluating issues in the experiment. There may be evidence of extraneous variables (not previously recognised) or confounding factors. Evaluation of the methodology based on evidence collected and suggested improvement(s) is a key section of the scientific report. This is discussed further in Module 1.12.

Record everything. Your data set may contain both quantitative (values and measurements) and qualitative (observations) data. Note any difficulties encountered or trials that were conducted slightly differently—perhaps a new source of a chemical was provided half-way through, a new measuring instrument was used or a different person was determining the readings. This information may be key to your analysis and evaluation. With justification, a data point can be identified as an **anomaly** and removed from the data set due to being an outlier. This may be due to a mistake or failure to correctly follow the method (see 'Processing the data' on page e85). Nevertheless, all values need to be recorded in the raw data table.

TABLE 1.10.3 Examples of sample size and their effect on an experiment

Example of analysed data	Effect of sample size on analysis
10 s of O_2 production from peroxidase at various temperatures  	Line graph with two sample points: With only two individual sample points, these results suggest an inappropriate relationship between temperature and enzyme activity; that enzyme activity increases with temperature.
10 s of O_2 production from peroxidase at various temperatures  	Line graph with three sample points using an uneven scale: The spread between the chosen individual sample points is inappropriate for this experiment as they should be evenly spread. This example produces results with an incorrect relationship between temperature and enzyme activity; that enzyme activity increases then begins to level off as temperature increases.
10 s of O_2 production from peroxidase at various temperatures  	Line graph showing limited sample points: The chosen number of individual sample points is appropriate. This may be sufficient; however, the next example provides more precision and validity for the relationship.
10 s of O_2 production from peroxidase at various temperatures  	Line graph with appropriate number and distribution of sample points: The number of individual sample points here best demonstrates the relationship between the variables.
10 s of O_2 production from peroxidase at various temperatures  	Line graph based on data that had no replicates (only one trial): These results are due to only a single trial for each individual sample point (distance) without any replicates. In this example, the measurement at 40°C was a mistake, and without replicates, such mistakes will influence the results.

Choosing not to record certain measurements or observations is invalid, shows bias and is scientifically fraudulent. Quality scientific analysis processes the raw data as it is and is open to any result. Module 1.11 describes how precision and validity can be assessed using calculations such as the percentage error, the percentage uncertainty and the uncertainty of the mean.

A workable plan for data collection is for one group member to be responsible for recording the data. This minimises clutter at the experimental work bench and provides a consistent single data set to share with the group. The recording person should add the measurement uncertainty of each piece of equipment or instrument as a range of data next to the measured value (e.g. measurement ± Δ measurement). Conducting the experiment and collecting data is a group activity; however, all subsequent parts of the task (data processing, analysis, evaluating and concluding) are completed individually. Therefore, it is important that the data set is disseminated to the group immediately after the experiment finishes.

Electronic data acquisition in schools

Electronic data acquisition takes advantage of highly accurate sensors to collect data directly for processing by a computing device (Figure 1.10.4). There are many sensors, probes and instruments available that can measure a vast variety of phenomena in a single device.

FIGURE 1.10.4 Data-acquisition software produces real-time graphs that can be downloaded or printed

Many smartwatches (Figure 1.10.5) and apps in phones include digital sensors and **data loggers** that can be accessed and used for some class practicals and experiments.

Recording is done accurately and can be continuous or manual, and the measurements are saved electronically. The saved measurements can then be accessed via a computer or directly from the tablet screen. The rate at which measurements are recorded is called the sample rate. The data capture rate can be varied from 100 000 times per second to once an hour.

FIGURE 1.10.5 Many smartwatches and phones have digital sensors and in-built data loggers

PUTTING IT ALL TOGETHER

The sample experiment report that follows covers the ISMG criteria. Use this as a model for reference.

Management of risks

Potassium chloride solution at this concentration (48 g/100 g, 6.4 mol L^{-1}) poses no significant risk, but eyewear should still be used to prevent eye contact with the powder (Risk Assess, 2022).

Handling glassware and a glass thermometer carries inherent hazards and may lead to personal injury. Thus, it is crucial to handle equipment with care, and any breakage should prompt immediate notification of a teacher. Additionally, solutions should be placed at the centre of the table to minimise the risk of breakage.

Using a hot plate to heat the water bath poses a risk of electrocution. To mitigate this, spillages should be avoided, and the water bath should be positioned centrally on the hot plate. In case of spillage, immediately alerting a teacher is necessary.

There are no ethical or environmental risks.

Results—raw data

TABLE 2 Temperature at which KCl precipitated (raw data)

		Temperature precipitation occurs (±0.5°C)				
		Trial				
Concentration of KCl (g/100 mL)	**Concentration of KCl (g/5 mL)**	**1**	**2**	**3**	**4**	**5**
36	1.8	28*	35.5	37	36.5	38
40	2	49.5	48	51.5	52	48.5
44	2.2	67.5	65	64.5	64.5	64
48	2.4	77	75.5	78	74.5	77.5

*significantly different trial; was removed from all calculations

1.11 Analysing

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- process data using a range of mathematical calculations
- present sample calculations
- analyse data to prepare graphs and identify trends
- analyse data to identify precision of evidence (using uncertainty) and accuracy of evidence (using percentage error).

PROCESSING THE DATA (SAMPLE CALCULATIONS)

Processing the data in numerous ways (including mathematical techniques and graphing) allows elucidation of relationships between variables. You will analyse trends or patterns in the data, uncertainties and limitations, outliers and results of significance. To prepare your **processed data**, you should consider which of the following mathematical techniques are suitable in your investigation:

- mean
- gradient analysis
- scatter plot (with best-fit lines, maximum and minimum trendlines and R^2)
- measurement uncertainty (absolute measurement uncertainty and percentage measurement uncertainty)
- propagation of measurement uncertainty (addition, subtraction, multiplication, division)
- uncertainty of the mean (absolute and percentage), $\Delta\bar{x} = \pm \frac{(x_{max} + x_{min})}{2}$
- percentage uncertainty (%) $= \frac{\text{absolute uncertainty}}{\text{measurement}} \times \frac{100}{1}$
- percentage error (%) $= \left|\frac{\text{measured value} - \text{true value}}{\text{true value}}\right| \times \frac{100}{1}$

These eight calculations are explained in Part A: Working scientifically and in the Science Inquiry section of the syllabus.

When you have decided which of these eight calculations are valid for your investigation, prepare a processed data table and include a sample calculation table that shows a single calculation for each. Remember, there are two types of uncertainty—one associated with the measuring equipment (measurement uncertainty) and one associated with the range of trials (uncertainty of the mean). Both of these values can be expressed in the same units as the value they describe (absolute uncertainty) or converted to a percent of the measurement or mean that they describe (percentage uncertainty). See Table 1.11.1.

TABLE 1.11.1 Example of processed data in a table

$CuSO_4$ conc. (M)	Mean cell potential (V)	Absolute measurement uncertainty (V)	Percentage measurement uncertainty (%)	Theoretical E_{cell} (V)	Absolute error (E)	Percentage error (%)
0.01	1.060	±0	±0	1.040	±0.019	±1.835
0.10	1.073	±0.005	±0.465	1.070	±0.003	±0.269
0.25	1.076	±0.005	±0.464	1.082	±0.005	±0.512
0.50	1.083	±0.005	±0.462	1.091	±0.007	±0.711
1.00	1.086	±0.005	±0.460	1.100	±0.013	±1.212

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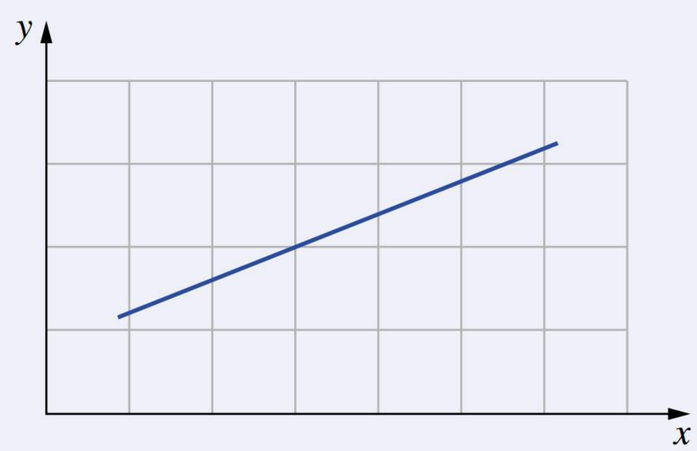
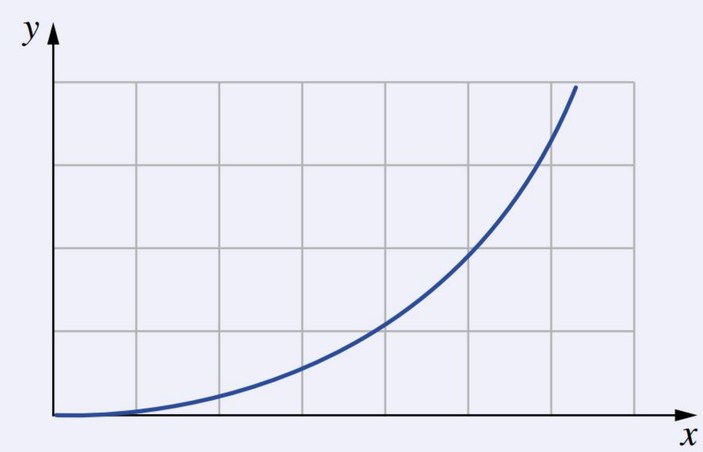
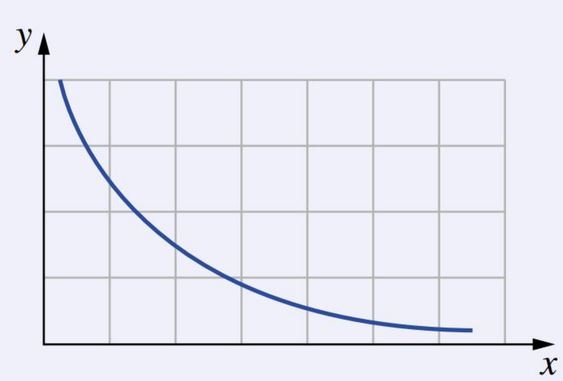
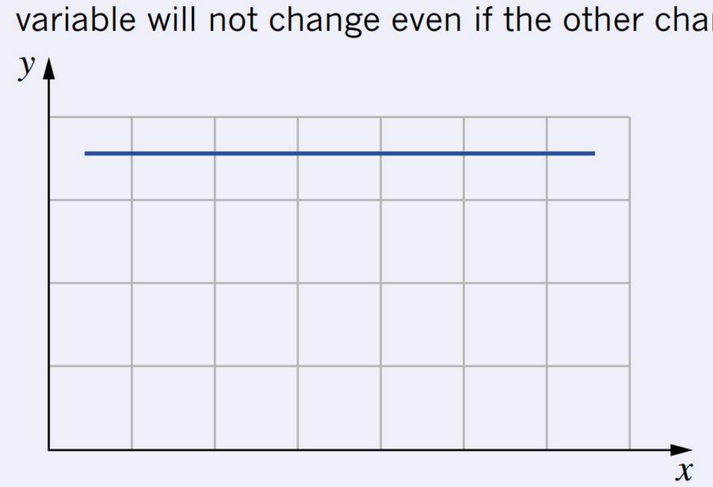
When calculations are performed with data values, the uncertainties associated with these values are combined in a process called propagating uncertainties. For example, if a density value is calculated using measured mass and volume and the relationship density = $\frac{\text{mass}}{\text{volume}}$, then the percentage uncertainty for the measurement of mass (using a weighing balance) is added to the percentage uncertainty for the measurement of volume (using a measuring cylinder). This total gives the percentage uncertainty for the density (see Module 1.5 for more details of measurement uncertainty).

IDENTIFICATION OF TRENDS, PATTERNS AND RELATIONSHIPS

There are a number of ways of presenting processed data, depending on its nature, including tables, graphs, flow charts and diagrams. Usually, a graph is most useful—a clear visual representation showing a direct or inverse relationship between the dependent and independent variables, and if the relationship is linear or not. A spreadsheet program will provide information about the trendline gradient and an R^2 value. By plotting expected values (if known) on the same graph, the accuracy of the data is visualised. A number of trends are shown in Table 1.11.2.

TABLE 1.11.2 Graphs showing different trends and relationships between variables

Variables that change in linear or direct proportion to each other produce a straight, sloping trendline. 	Variables that change exponentially in proportion to each other produce a curved trendline. 
When there is an inverse relationship, one variable increases as the other variable decreases. It may be (a) direct or (b) non-linear. **a** **b** 	When there is no relationship between two variables, one variable will not change even if the other changes. 

Plotting error bars or maximum and minimum trendlines on a graph indicates if the averages shown are significantly different. Overlapping error bars indicate that the difference between these two values is not statistically significant. The graph(s) that you have prepared provides evidence of the relationship between the dependent and independent variables; however, you should describe the features of the graph using a succinct statement such as 'as (independent variable) increases, (dependent variable) increases/decreases'.

It would be useful to follow this with some values from the graph to justify the occurrence of the trend. Further useful analysis could describe the gradient, R^2 value, similarity/difference to the expected values and whether the error bars overlap or not. Remember, the report has an evaluation section, so at this stage, it is not necessary to fully explain every aspect of the data. A 'thorough and appropriate identification of trend/patterns/relationships' is what is required here in the Analysis section.

IDENTIFY UNCERTAINTY AND LIMITATIONS OF THE EVIDENCE

Uncertainty, precision and reliability

In chemistry, there is always variation in measurements (the terms precision and uncertainty were explained in Part A). The level of uncertainty is indicated by:

- using values for the measurement uncertainty of the instrument(s) or
- using the range of trials and dividing by 2 (uncertainty of the mean).

Both of these can be expressed as a percentage of the value they describe, and both of these give us an indication of the level of random error in the experiment. When identifying and discussing the level of random error, it is most useful to calculate both of these and relate the discussion to the higher value, keeping in mind that, generally, a percentage uncertainty of 5% is the maximum value for a precise and reliable data set.

Consider these two uncertainty types in an example data set (Table 1.11.3), which shows the volume of 1.0 M hydrochloric acid required to neutralise 25 mL of an unknown concentration of sodium hydroxide solution. First, the uncertainty due to the precision of the burette (measurement uncertainty) is the smallest increment of the scale, i.e. ± 0.1 mL. When expressed as a percentage of the mean, this is 0.48%.

Second, the uncertainty of the mean is calculated using uncertainty of the mean = $\frac{\text{range}}{2}$, giving an uncertainty of ±0.4 mL. When expressed as a percentage of the mean, this is 1.95%. We see that the uncertainty of the mean is greater than the measurement uncertainty, so we can deduce that the precision of the measurement instrument is only slightly contributing to the level of random error in the experiment. There are further factors contributing to the 1.95% uncertainty.

In addition, as the 1.95% relative uncertainty of the mean is well below 5%, we can state that the data is precise and reliable, and that the level of random error in the experiment is low.

TABLE 1.11.3 Volume of 1.0 M hydrochloric acid required to neutralise 25 mL of an unknown concentration of sodium hydroxide solution. The mean is reported with its measurement uncertainty, 0.4 mL.

Trial	Volume of hydrochloric acid used (mL)
titration 1	20.6 ± 0.1
titration 2	20.9 ± 0.1
titration 3	20.1 ± 0.1
titration 4	20.4 ± 0.1
mean	20.5 ± 0.4

Percentage error, accuracy and limitations of the evidence

The rationale has provided background information that informs the relationship proposed in the research question. This provides your expected trend, and in your Analysis, you will state whether this trend was observed. In addition, you may be able to research expected values for the data set that you have collected. If this is the case, it is expected that you will calculate percentage error values for each independent variable data point.

Percentage error measures how different your data is to expected values, and so will allow you to make a judgement about accuracy and validity. Low percentage error indicates low systematic error in the investigation. By researching expected values, you are accessing experimental data from scientific laboratories, and so we expect that the equipment and methodology in a secondary school laboratory is unlikely to accurately replicate these values. For this reason, you cannot use '5%' as a guide for acceptable data (as for uncertainty and precision). Percentage error is likely to be higher than this. Nevertheless, if a percentage error value is as high as 50%, you can identify a lack of accuracy and the investigation is lacking validity—state this as a limitation.

Again, when identifying these issues as part of trends, patterns and relationships, resist the temptation to explain and suggest reasons for these results because this discussion is more relevant to the concluding and evaluation sections.

PUTTING IT ALL TOGETHER

The sample experiment report that follows covers the ISMG criteria. Use this as a model for reference.

TABLE 3 Sample calculations—the data processing strategy involves the following calculations, and the results of this processing are given in Table 4.

Calculation	Example using 48 g/100 mL KCl
Average $\frac{\text{sum of all values}}{\text{number of values}}$	$= \frac{77.0 + 75.5 + 78.0 + 74.5 + 77.5}{5} = 76.5°C$
Uncertainty of the mean $\frac{\text{maximum trial} - \text{minimum trial}}{2}$	$= \frac{78.0 - 74.5}{2} = 1.75$
Percentage uncertainty of the mean (%) $\frac{\text{uncertainty}}{\text{average}} \times 100$	$= \frac{1.75}{76.5} \times 100 = 2.29\%$ (2 dp)
Percentage error (%) $\frac{\text{experimental value} - \text{expected value}}{\text{expected value}}$	$= \left\lvert \frac{(76.5 - 67.5)}{67.5} \right\rvert \times 100 = 13.33\%$ (2 dp)
Percentage measurement uncertainty (%) (thermometer) (calculated using lowest average temperature, 76.5°C) $\frac{\pm 0.5°C}{\text{average}} \times 100$	$= \frac{\pm 0.5°C}{76.5} \times 100 = 0.7\%$ (1 dp)

TABLE 4 Processed data

Concentration of KCl (g/100 mL)	Average temperature (±0.5°C) (1 dp)	Theoretical temperature values for KCl (°C)	Uncertainty of the mean (°C) (2 dp)	Percentage uncertainty of the mean (%) (2 dp)	Percentage error (%) (2 dp)	Percentage measurement uncertainty (%) (1 dp)
36	36.8	26	±1.25	±3.40	±41.54	±1.4
40	49.9	40	±2.00	±4.00	±24.75	±1.0
44	65.1	55	±1.75	±2.69	±18.36	±0.8
48	76.5	67.5	±1.75	±2.29	±13.33	±0.7

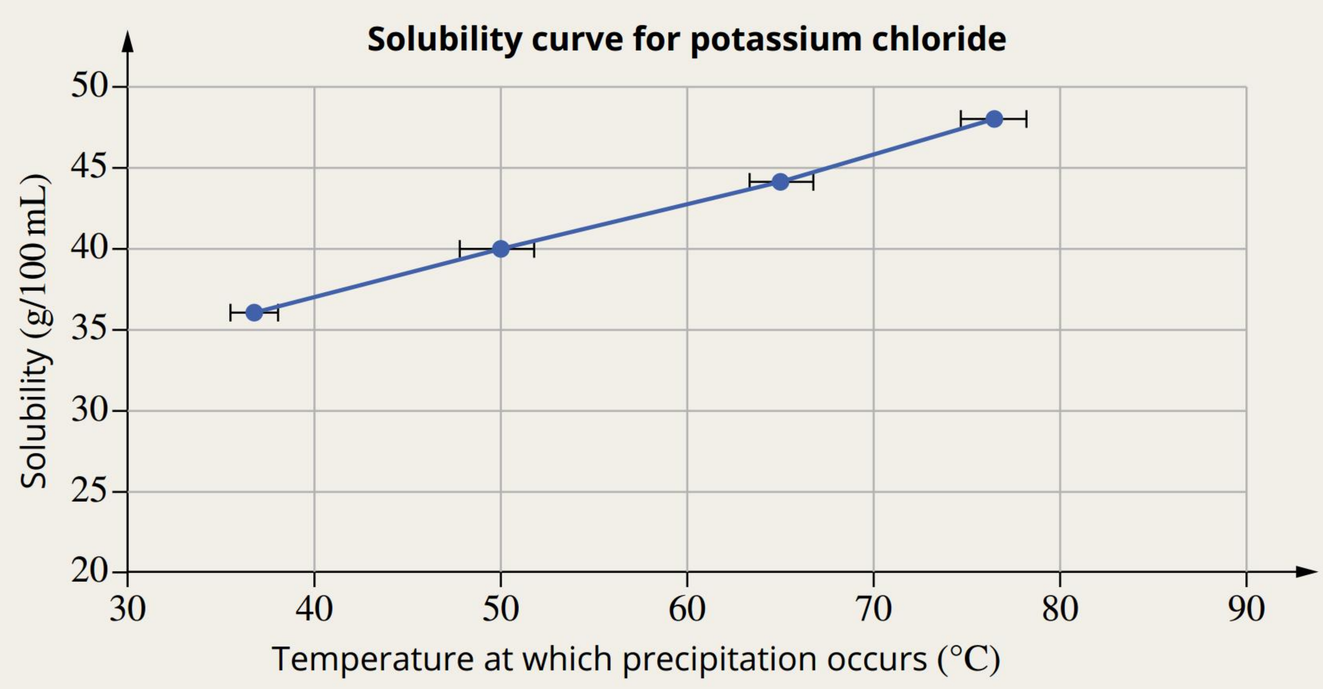


FIGURE 5 Solubility curve of KCl using the average values with error bars (± uncertainty)

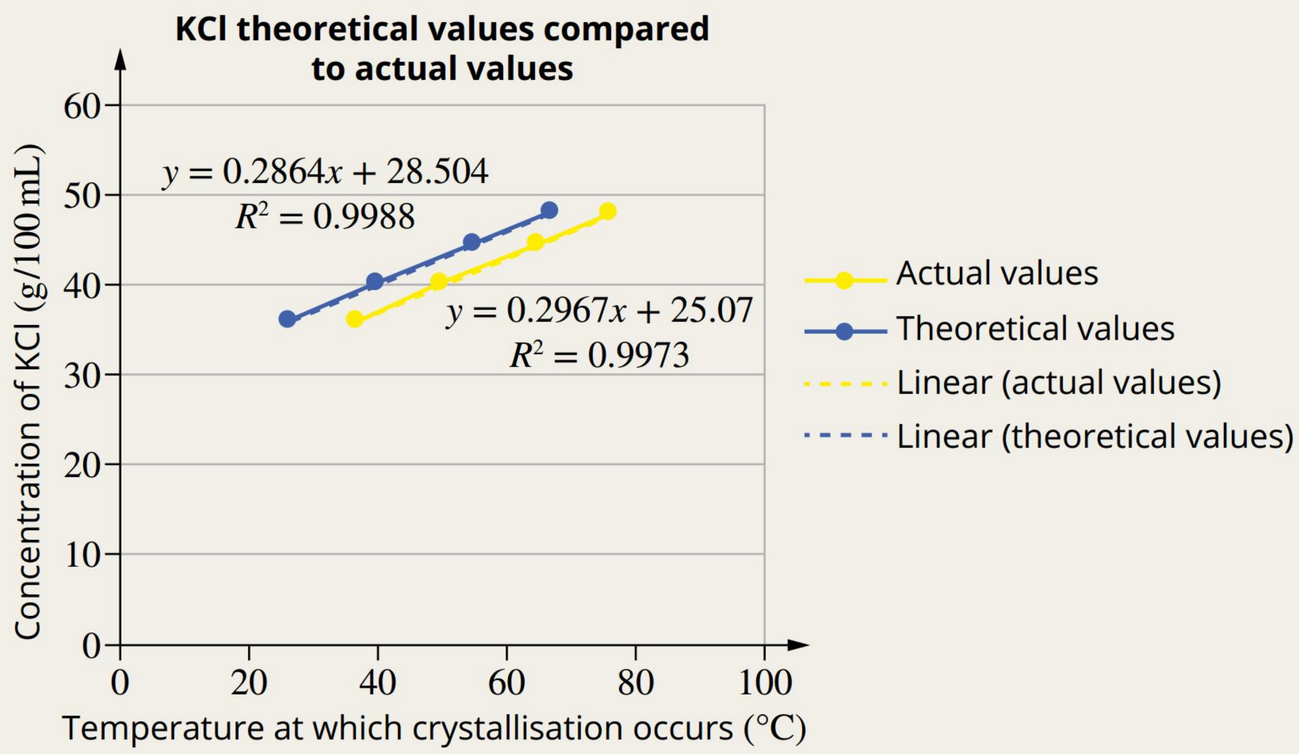


FIGURE 6 KCl theoretical values compared to derived data (Wikipedia, 2022)

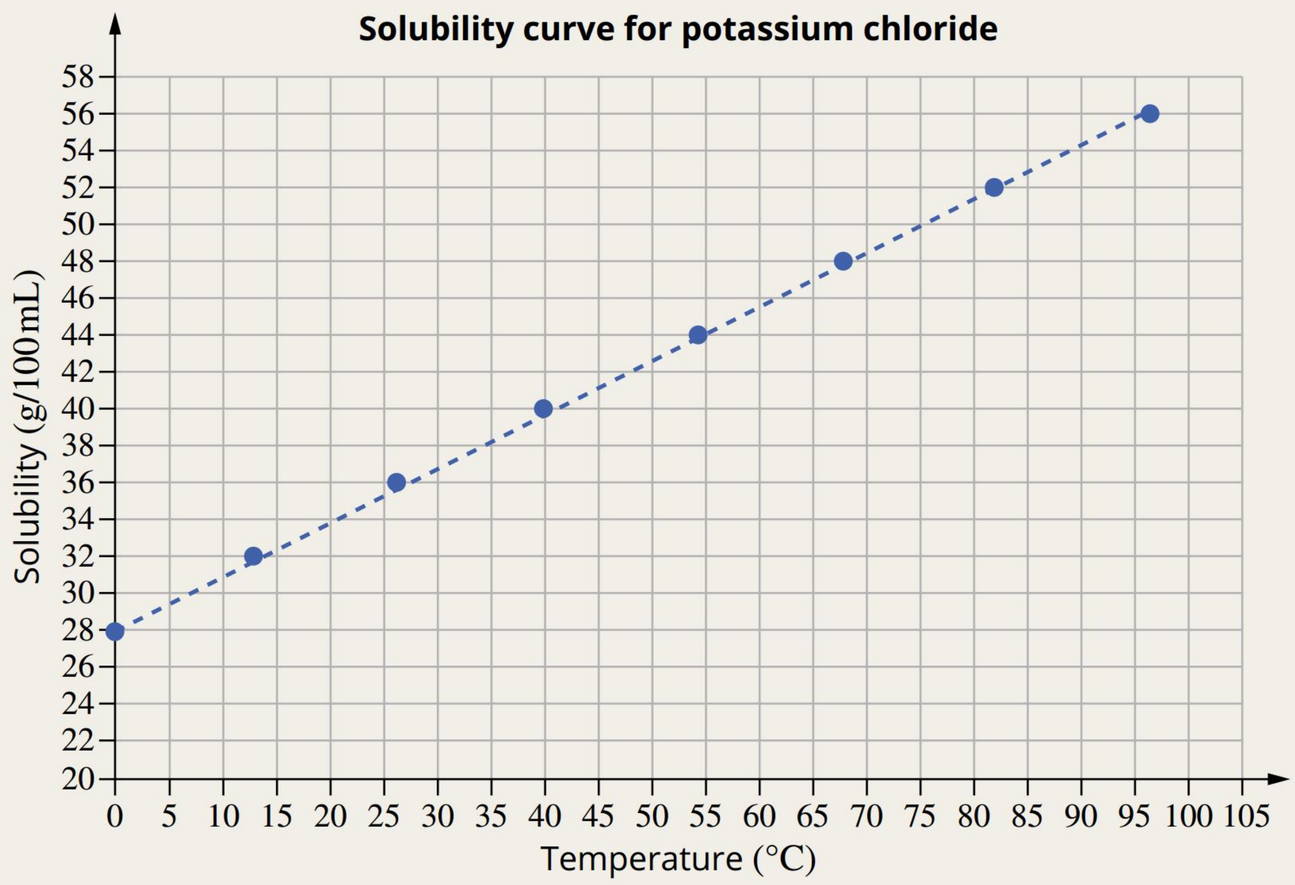


FIGURE 7 KCl theoretical values (Wikipedia, 2022)

Analysis

The solubility trend observed for KCl was that as concentration increased, so did the temperature of crystallisation. Figure 5 illustrates this pattern: precipitation occurred at 36.8°C for 36 g/100 mL and rose notably to 76.5°C for 48 g/100 mL. These findings are similar to theoretical values (Figures 6 and 7), although experimental temperatures were higher than theoretical values for each concentration used. This means that measured solubilities were lower than expected for all concentrations. The data displayed a strong linear trend with R^2 value exceeding 0.99.

Uncertainty of the mean was minimal, ranging from 2.29% to 4.00%, indicating low random error and precise experimental data, as the values were all below 5%. This indicates reliable data. Non-overlapping error bars in Figure 5 suggest that the averages are significantly different. Measurement uncertainty of the thermometer was also minimal, ranging from 0.65% to 1.36%.

However, data contains limitation(s) because accuracy was compromised by substantial discrepancies between theoretical and actual results, with percentage errors ranging from 13.34% to 41.54%. This hints at systematic errors in experimental design, potentially affecting data validity and limits its use in answering the research question. Additionally, the narrow concentration range tested (36 g/100 mL to 48 g/100 mL) could limit the generalisability of findings, a point to be explored further in the evaluation. There was only a 3.6% difference in the gradients of experimental versus theoretical data sets, indicating the systematic error that was present changed little throughout the experiment.

1.12 Interpreting and evaluating

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- formulate a conclusion linked to the research question using interpretation of evidence
- justify your conclusion
- evaluate reliability and validity and justify your arguments with evidence
- suggest improvements and extensions.

In order to be awarded a 5 for Interpreting and Evaluating, you need to present a justified conclusion, a justified discussion of the quality of the experimental process and suggest improvements and extensions derived on the analysis of the evidence.

JUSTIFIED CONCLUSION LINKED TO THE RESEARCH QUESTION

While you have already described the trend observed in the data (Analysis), it is important, in the conclusion, to extend this idea further to relate specifically to the research question. In an objective and clear manner, state the observed relationship between the dependent and independent variables using the terminology of the research question. Consider the following:

- was the research question supported?
- has the research question been fully answered? (If not, identify why not.)

Table 1.12.1 shows examples of concluding statements.

TABLE 1.12.1 Strong and weak conclusions to a research question and hypothesis

	Strong conclusion	Weak conclusion
Research question: How does the temperature affect the pH of water?	Analysis of the results on the effect of an increase in temperature of water from 5°C to 40°C showed an inverse relationship in which the pH of water decreased from 7.4 to 6.8. These results support the current knowledge that an increase in water temperature results in a decrease in its pH.	The results show that temperature does affect the pH of water.
Hypothesis: An increase in the temperature of pond water will result in a decrease in the measured pH of the water sample.	An increase in temperature from 5°C to 40°C resulted in a decrease in the pH of the water from 7.4 to 6.8.	The pH of water decreased as temperature increased.

There are several ways to justify the conclusion, including but not limited to:

1 describing the chemical concepts (scientific understanding and theory) that explain the observed relationship.

The key finding should be explained within the right context, meaning the related chemical ideas, concepts and theories. Does the data support or contradict the literature? Within this context, explain the basis for the trend observed.

2 describing the evidence that led to the data trend.

State values that indicate the strength of the relationship between the experimental variables (data, observations or results), including information gained from the error bars on the graph and the R^2 value(s). Refer to your tables/graphs to cite evidence.

3 comparing your findings to secondary data you have found from journal articles or other reliable sources that are directly connected to the experiment.

Explain whether your observations support the published results. You should report that your results are consistent with the published data, or reflect on the contrasting results and identify or suggest possible reasons for the difference. This could be due to differences in the measurement technique or other factors such as the control or measured variables. It might also help you identify possible sources of error within your investigation.

In circumstances where a clear trend is not discernible, you can interpret what the results mean. Interpretations are made when limitations exist related to the methodology employed, the sample size, the instruments used, the variables controlled and the raw data measured. Interpretations are not meant to provide answers and comprehensive explanations, only a valid and reliable plausibility based on what was measured.

In the conclusion, it is appropriate to briefly describe evidence relating to the quality of experimentation and any key limitations. You have two aspects (already identified in Analysis), reliability and validity (as described by percentage uncertainty and percentage error, respectively). Describe which of these was high/low and what this indicates about reliability and validity. Resist the temptation to explain these further as this is more usefully done in the Evaluation.

The conclusion is sometimes positioned after the analysis and sometimes at the end of the report. Its placement in your report will need to make sense to you and maintain the flow of ideas.

- Option 1: planning → data collection and analysis → conclusion → evaluation
- Option 2: planning → data collection and analysis → evaluation → conclusion

JUSTIFIED DISCUSSION OF RELIABILITY AND VALIDITY

Your analysis and conclusion have identified the trend in the data but also identified two other key aspects of the data—reliability and validity. A statement of these has also been made in the conclusion. The verb in analysis is 'identify', but here (in Interpreting and Evaluating) the cognition is 'discuss'. This means that you must explain statements made in the analysis related to percentage uncertainty (reliability) and percentage error (validity). In your discussion, consider the following:

- are these low or high?
- what is the effect on the usefulness of the data to answer the research question?
- what could have caused excessive uncertainty and random error?
- what could have caused excessive systematic error?
- what factors could affect validity, accuracy, precision and reliability of data?

As you write the discussion, remember that your data processing has provided extensive evidence—not just the independent–dependent variable relationship but also measurement uncertainty, uncertainty of the mean and percentage error. Use these values to add depth to your discussion and use evidence rather than methodology to describe and discuss uncertainty and limitations in the investigation. For example, if you have calculated the percentage uncertainty associated with the measurement instrument (say, a measuring cylinder) to be 0.24%, then suggesting that the lack of precision of this equipment is the cause of a percentage error of 40% is not reasonable.

A second example of the use of evidence relates to percentage error. If you have calculated the percentage error of the data to range between, say, 30% and 50% and also shown that the percentage error decreased during the experiment, your reasoning for the cause of this percentage error needs to relate to a factor that is less at the end of the experiment than at the beginning. An example of this is a galvanic cell experiment where an electrode becomes slightly oxidised in the electrolyte solution during the experiment—the resistance of the circuit increases with oxidation. As a result, we expect the systematic error to increase during the experiment, and so percentage error should increase not decrease. A proposed systematic or random error should be evident in the data for the syllabus descriptor 'justified discussion of validity' to be met.

As you discuss factors affecting the quality of the data, remember the definitions of random and systematic error and describe each factor in terms of one of these. Is the factor expected to always produce a change in the same direction (systematic error, low validity)? Or will the factor produce a more random effect where the value is sometimes higher and sometimes lower (random error, low reliability)? Look carefully at the evidence in your data for each of these. Refresh your understanding of random and systematic errors using Figure 1.12.1.

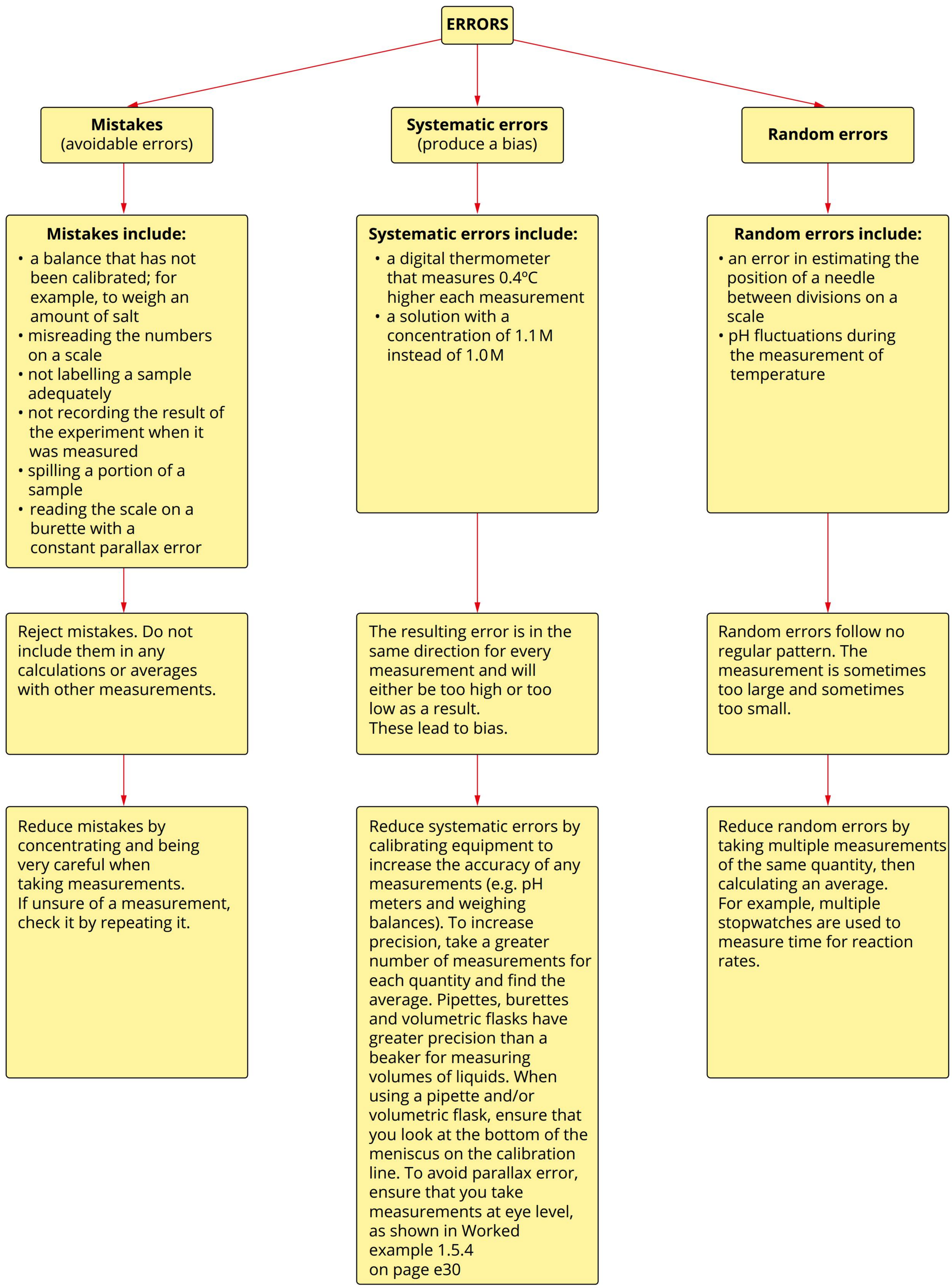


FIGURE 1.12.1 Types of errors that can be made in an experiment

One form of systematic error is **bias** in sampling or measurements. Bias can result from poor definitions, incorrect assumptions, misunderstandings between group members and failure to use equipment correctly. Some biases cannot be eliminated but should at least be addressed in the discussion.

IMPROVEMENTS AND EXTENSIONS

Once any limitations or problems in the methodology have been identified, recommend improvements for how the investigation could be conducted if repeated. Some guiding questions are:

- has my research question been fully answered and what evidence is further required to answer it?
- what improvements can be made to aspects of the investigation identified as limitations?
- what changes to the materials or method would address the lack of reliability or validity of the data?

Questions to consider when suggesting extensions to this student experiment could include the following:

- do the findings lead to further questions?
- can the findings be extended to another situation?
- what extensions can be investigated for a related scientific idea?
- do the experimental findings have broader or further practical implications?

In the Modifications section, you provided a reason for each change that you made to the original experiment. In a similar way, provide a reason for each improvement and extension. In order to demonstrate that the extensions are logically derived from the analysis of the evidence, you need to provide a reason for each extension and how it relates to the evidence. Similarly, how the suggested improvements would have addressed or overcome the limitations that were identified earlier. Statements such as 'test more substances' or 'complete more trials' do not match a high-level response ('logically derived' ISMG descriptor) and will better match lower descriptors ('related' or 'ineffective').

The syllabus descriptor states 'logically derived', so it is important to limit your suggestions for improvements and extensions to experimental issues that have already been identified (in analysis and evaluation). Conversely, if you have described a key limitation of the experiment related to high levels of random or systematic error, you should describe improvement(s) for this issue.

PUTTING IT ALL TOGETHER

The sample experiment report that follows covers the ISMG criteria. Use this as a model for reference.

Conclusion

It was found that increasing concentrations of KCl (36 g/100 mL, 40 g/100 mL, 44 g/100 mL and 48 g/100 mL) correspondingly raised the temperature at which crystallisation took place (see Figure 5). For instance, precipitation occurred at 36.8°C with a KCl concentration of 36 g/100 mL, and at 76.5°C with 48 g/100 mL. This trend is due to increased thermal energy at higher temperatures, which increases particle movement, which in turn increases collisions between particles of solute and solvent and weakens the existing bonds between particles. Specifically, water molecules, due to their polarity, attract ions from KCl, causing its cations and anions to separate at higher temperatures. Upon cooling, the reduced kinetic energy prompts crystallisation of the solute as ions have less movement and greater ability to reform ionic bonds between K^+ and Cl^- (lattice reforms).

The experiment exhibited high reliability (2.29–4.00% uncertainty, low random error) but low validity (13.33–41.54% error, high systematic error). Thus, addressing limitations (mostly systematic error) is crucial for accurately answering the research question.

Evaluation

The method employed in this experiment demonstrated reliability, evidenced by consistently low percentage uncertainty and measurement uncertainty (Table 4). This indicates minimal random error and suggests

reproducibility of results by other researchers. To further reduce uncertainty, expanding the range of samples could help refine data and identify outliers.

However, the method's validity is compromised by significant percentage errors ranging from 13.33% to 41.54%, particularly notable at 36 g/100 mL of KCl (41.54%). All temperatures recorded were higher than expected—this means that KCl in the current experiment showed solubilities lower than expected. As the gradients of the trendlines were similar, there is evidence of systematic error(s). This could possibly be due to challenges in determining complete dissolution in the water bath—if the solution still contained undissolved crystals at the start of the experiment, crystallisation could be accelerated. Also, it was difficult to see the small crystals as they were appearing because the test tube had water on the outside. However, this difficulty is unlikely to have caused the systematic error of a too-high temperature because the difficulty in seeing the crystals would likely cause a too-low temperature reading due to a delayed reaction time in recognizing crystallisation. Other inconsistencies could have resulted from varying times the tubes were in the water bath, and so varied evaporation levels among test tubes. This might influence concentration and subsequent precipitation temperatures unpredictably.

Improvements and extensions

To improve this experiment, a dark paper background could be used during dissolving and also during crystal detection to make sure the solute is first fully dissolved and secondly detected at the correct time. Additionally, to avoid excess evaporation while in the water bath, immersion times for test tubes should be standardised and a loose stopper should be used, thereby improving methodological reliability and data accuracy.

Furthermore, the limited range of concentrations (four tested concentrations) limits the full identification of the trend. Increasing the number of concentrations would provide a more comprehensive data set, enabling more confident trend analysis and better comparison with theoretical values.

A suitable extension to this investigation would be to investigate the solubility of a potassium compound with an even larger anion (e.g. MnO_4^-). Comparing the current data to the original experiment shows that decreasing the size of the anion (NO_3^- to Cl^-) decreases the solubility. This trend could be due to steric hindrance within the lattice—the lattice is stronger when the anion and cation are about the same size (Holmes et al., 2019). KCl is shown to have a lower solubility than KNO_3—using this trend, we would expect $KMnO_4$ to have a higher solubility than both KCl and KNO_3. On the other hand, determining the solubility curve for lead nitrate or sodium nitrate could further explore the effect on solubility of changing the cation (not anion) in an ionic compound.

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PART C RESEARCH INVESTIGATION (IA3)

The research investigation assessment requires students to investigate a claim, provided by their teacher, by drawing on secondary evidence from scientific texts. Students will draw on research to analyse, interpret and evaluate the evidence to reach a justifiable conclusion about the research question. The task requires students to locate and use information beyond the scope of their knowledge and the data they have been given.

The QCAA Chemistry 2025 General Senior Syllabus states that students must work individually to develop and investigate their own research question.

The research investigation constitutes 20% of the total subject score and may be presented in:

- written form of up to 2000 words or
- multimodal form using at least two modes delivered simultaneously and up to 11 minutes.

INSTRUMENT-SPECIFIC MARKING GUIDE

As with the student experiment, responses are assessed against an instrument-specific marking guide (ISMG). In developing the research report, it is important to keep in mind the assessment objectives, particularly the characteristics that are described in the performance level descriptors.

The ISMG has four criteria: Forming and finding, Analysing, Interpreting and Evaluating.

Each criterion has performance levels, against which the qualities of the response are assessed.

A performance level is comprised of a performance level descriptor and mark (or range of marks).

The performance level descriptor describes the characteristics that are demonstrated by a response of that quality.

In this part, each stage of the development of the research investigation will be discussed and aligned with the relevant ISMG criteria, and elaborations for the highest performances.

The research question should specifically address one of the concepts associated with the claim. Commence by identifying a claim and developing your own research question based on that claim. Since this assessment relies heavily on access to research, students need to be able to easily find sources relevant to the research question. Throughout the process, be mindful that scientific language and representations are used (refer to Module 1.8 for more information).

1.13 Forming and finding

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand and select a claim
- classify elements of the claim
- unpack the elements to identify variables, terms and concepts related to the claim
- plan research and locate sources relevant to the claim
- distinguish between primary and secondary sources
- locate a range of primary and secondary sources
- use a scientific journal to record the information in the sources
- refine the concepts to develop an investigable research question
- understand the criteria against which the research investigation will be assessed.

The ISMG for the Forming and finding criterion, as shown in Table 1.13.1, is assessed in relation to the development of the research question from the claim and the communication of the findings of the investigation through a scientific report.

TABLE 1.13.1 The performance characteristics associated with the highest performance level of the Forming and finding criterion

Criteria	Assessment objectives	Performance characteristics	Marks
Forming and finding	1. Describe ideas and findings about the properties and structure of organic materials or chemical synthesis and design.	• a considered rationale identifying clear development of the research question from the claim • a specific and relevant research question • selection of sufficient and relevant sources • appropriate use of genre conventions • acknowledgement of sources of information through appropriate use of referencing conventions	5
	2. Apply understanding of the properties and structure of organic materials or chemical synthesis and design to develop research questions.		
	6. Investigate phenomena associated with the properties and structure of organic materials or chemical synthesis and design through research.		

There are three aspects to the Finding and forming criterion.

To achieve the highest mark (5) in the Forming and finding criterion, you need to create a research question clearly linked to the Unit 4 subject matter that identifies measurable independent and dependent variables, as well as a control variable-specific research question. Then you need to construct a rationale that clearly outlines how the research question is developed from the original claim. A research rationale outlines the reason to conduct research on your chosen claim, i.e. it is the justification for the investigation. This is achieved by conducting a thorough literature review to understand what is already known in the chosen topic and to identify the concepts from Unit 4 that are related to the topic. Students who explain concepts outside the syllabus in their Rationale struggle to stay within the word limit.

Finally, the structure and style of the report, quality of sources and use of referencing are assessed.

UNDERSTANDING THE NATURE OF A CLAIM

A claim is an assertion made without any accompanying evidence to support it. The claim can be a sentence, statement within a sentence, title of an article, quote or anything published in any form. The claim should be in isolation from any justification using data, research, evidence or reasoning from known information to support it. The claim is a broad statement that can encompasses a range of related topics and relationships.

SELECTING A CLAIM

If you are provided with a choice of claims, you should ask yourself the following questions about the claims.

Which claims:

- interest me or are most relevant to me?
- are easy to break down and link to the subject matter in the unit?
- are broad enough to allow me to undertake a unique investigation?

The answers to these questions will help you decide on the most appropriate claim for you.

To develop the research question from a claim, students must analyse, understand and identify one or more of the following:

- known scientific concepts
- variables
- measurable terms
- ideas related to concepts
- a term that is stated to influence another.

Record the information you collect, your thoughts and your analysis in a hard copy or electronic scientific journal. When you write the report, this information will be useful in writing the rationale that documents how the research question was developed from the claim. Write down all the elements found in the claim and try to categorise them using the list above. Each element within the claim may suit more than one category. Table 1.13.2 outlines three examples of analysing and categorising elements of a claim.

TABLE 1.13.2 Three examples of analysing and classifying elements of a claim

Example claim 1: Plastics are bad for the environment.		
Elements	**Classifying elements of the claim**	**Unpacking the elements**
• Plastics are made from crude oil.	• a term that is stated to influence another	• hydrocarbons
	• a term that is stated to influence another	• polymers
	• ideas that relate to concepts	• non-renewable resource
	• measurable terms • variables	• manufacture requires lots of resources/energy
• Plastics are disposed of and not recycled.	• known scientific concepts	• all plastics can be recycled but not all are waste
• Plastics release toxic chemicals.	• ideas that relate to concepts	• breakdown in environment
	• known scientific concepts	• chemicals released from combustion additives
• Plastics are not biodegradable.	• measurable terms	• polymers are inert
	• ideas that relate to concepts	• not easily broken down in nature by air, water, sunlight

Example claim 2: Natural shampoos are better than commercial shampoos.		
Elements	**Classifying elements of the claim**	**Unpacking the elements**
• Define the term 'better'.	• measurable terms • variables	• more environmentally friendly
	• ideas related to concepts • variables	• better cleaning efficiency
• Natural shampoos do not contain harmful chemicals.	• a term that is stated to influence another	• synthetic chemicals are toxic
• Natural shampoos clean as effectively as commercial shampoos.	• known scientific concepts	• how surfactants work
	• measurable terms • known scientific concepts	• cleaning effectiveness is measurable and related to surface tension, wetting time, solid content, foaming ability

Example claim 3: Green chemistry is clean chemistry.		
Elements	**Classifying elements of the claim**	**Unpacking the elements**
• Green chemistry	• a term that is stated to influence another	• green solvents
	• ideas related to concepts	• preventing pollution
	• ideas related to concepts	• renewable energy
	• a term that is stated to influence another • measurable terms • variables	• atom economy—more effective synthetic reaction
	• a term that is stated to influence another	• renewable materials
• Environment	• measurable terms • variables	• fewer pollutants released
	• measurable terms • variables	• fewer resources required
• Clean chemistry	• ideas related to concepts	• non-toxic
	• measurable terms • variables	• less energy required
	• measurable terms	• reduced reagents

LOCATING SOURCES

It is important to recognise that this is not a university-quality report as students do not have the time, access or understanding to analyse the information provided in the scientific research journals. In addition, the research investigation is limited to 2000 words, so does not allow for the depth of investigation in a research journal.

When gathering scientific evidence for the research investigation, source it from reputable publications including:

- scientific journals, research papers and scientific reviews
- scientific articles written by organisations who apply scientific research to their industry
- commercial articles such as those in science magazines, newspapers and websites.

The research investigation must include a reference list of sufficient and relevant sources. *Sufficient* is defined as 'enough or adequate for the purpose', and *relevant* as 'bearing upon or connected with the matter in hand; to the purpose; applicable and pertinent; having a direct bearing on'. Figure 1.13.1 points out the features of sources deemed *sufficient* and *relevant*.

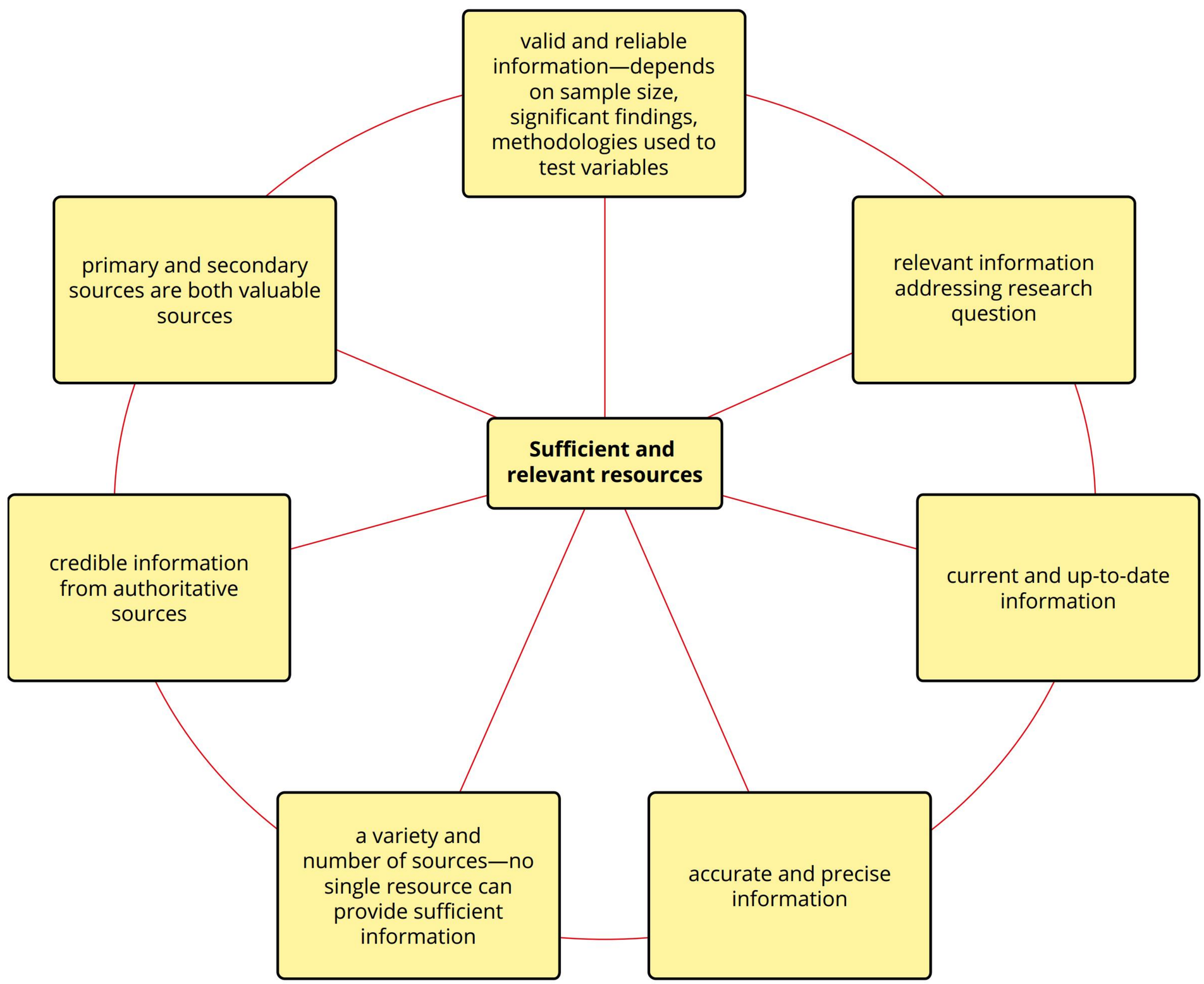

FIGURE 1.13.1 Features of sources suitable for the research investigation

A good place to start research is to look for interesting sites and textbooks to identify relevant keywords and concepts rather than immediately searching for complex research articles. This could include videos, general scientific articles and even Wikipedia to gain a general understanding of the topic.

Access available open-access sources, some of which can be identified using Google Scholar, educational, government or industry websites, with suffixes including .edu, .gov or .org.

You can often freely access scientific journals through academic networks, such as ResearchGate and Academic.edu. If the article has not already been published, you can request a copy of the article from the author or ask them a question.

When accessing the sources, start with the title, which should include some of the keywords related to the concept. As you refine the focus of your investigation, use the evidence to refine the claim and develop the rationale. Your search will narrow and lead to data tables, graphs, images and abstracts. If the abstract is useful, download the article or request a copy of it. Look at the images and conclusion. These may be more useful than the text of the article.

Remember to document the sources and summarise the information contained in your journal to facilitate the writing of the report and generate a reference list.

A useful way to collate the evidence is in a table with headings such as:

- Article overview, which summarises the article
- Evidence, which outlines the methodology, trends/patterns/relationships and limitations
- Conclusions, which summarises the evidence
- Relationship to research question, which includes your thoughts and highlights the parts of the research question that this evidence addresses
- Limitations, which identifies aspects of the research question that are not addressed or cannot be answered due to the methodology.

Consider whether the information you use is from a primary or secondary source.

Primary and secondary sources

Table 1.13.3 summarises the characteristics of primary and secondary sources. Sometimes, the same information may be contained within a primary and a secondary source, depending on when and by whom it was written. For example, a scientist's journal article on a clinical trial of treatments for teenage obesity is a **primary source**, while a general magazine article about teenage obesity, written by a journalist and referring to the scientific study, is a **secondary source**.

TABLE 1.13.3 Summary of primary and secondary sources

	Primary sources	Secondary sources
characteristics	• first-hand records of events, experiences, experimental data • written at the time the event happened • original documents	• interpretations of primary sources • written by people who did not see or experience the event • use information from original documents but rework it
examples	• results of experiments • scientific journal/magazine articles • reports of scientific discoveries • photographs, specimens, maps and artefacts • interviews with experts • websites (if they meet the criteria above)	• textbooks • biographies • newspaper articles • magazine articles • radio and television documentaries • websites that interpret the scientific work of others • podcasts

A primary source is written by the observer or witness of an event or the scientist who conducted the research. The information has only been processed by the original observer; therefore, it is the least biased of all available sources of information. However, even primary sources may be biased, as the observer or researcher had to make choices related to the observation, control of variables, use of instruments and choices for processing data.

Secondary sources of information are not eyewitness accounts but interpretations of events by other people. As second-hand information, accuracy and reliability may be reduced, and events may be interpreted through the writer's perception and bias. You should aim to use a wide range of data sources when using secondary data, to cross-check for accuracy, reliability and validity of information.

When searching for information and evidence, follow these guidelines.

1 Determine if it is a primary or secondary resource.

2 Confirm that it is valid.
   - **a** Check that it contains information that is specifically related to the claim.
   - **b** Check that the evidence and information are pertinent to the variables in the research question.

3 Assess its reliability.
   - **a** Is it current/recent information?
   - **b** Is it up-to-date in its understanding of relationships?
   - **c** Is the evidence equivalent to other sources?
   - **d** Check credibility—consider who the author is, their qualifications and expertise.
   - **e** Evaluate the methodology, including what variables were controlled or measured.

Articles in scientific journals

Peer-reviewed scientific journals are excellent sources of information. Journals are a collection of scientific reports written by scientists who conducted research. The reports and articles found in scientific journals are published primary sources, meaning they are the results of the experiments (Figure 1.13.2).

Polymer Chemistry

PAPER

Cite this: Polym. Chem., 2024, 15, 2070

Solvent effects on surface-grafted and solution-born poly[N-(2-hydroxypropyl)methacrylamide] during surface-initiated RAFT polymerization †

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rsc.li/polymers

The difference in the molar mass between surface-grafted and solution-born polymers grown during surface-initiated (SI) polymerization has caused controversy for years. To understand it, we study the solvent effects on the polymer formed on the surface and in the solution by investigating their macromolecular parameters. We utilized reversible addition fragmentation chain-transfer (RAFT) polymerization to grow surface-grafted and solution-born poly[N-(2-hydroxypropyl)methacrylamide] (p(HPMA)) under different solvent conditions. Changing the solvent proticity and/or polarity in fluences the solution propagation rate, leading to mass transfer limitations and a concomitant discrepancy in the molar masses of the polymer formed in solution and grafted from the surface. Moreover, the solvent effects were found to directly determine the grafting density of surface-grafted p(HPMA). These results highlight how decisive the solvent effects on the SI-RAFT polymerization of HPMA are and that they may be key to regulate the physical and macromolecular parameters of the obtained surface-grafted p(HPMA) brushes.

Introduction

Poly[N-(2-hydroxypropyl)methacrylamide] (p(HPMA)) represents the state of the art of biocompatible, non-toxic, and non-immunogenic polymers and has found extensive use in drug delivery.[1–4] Its polymer brush coatings on surfaces inhibit non-specific protein binding (fouling) in various biomedical applications.[5–8] P(HPMA) brushes showed outstanding hemocompatibility and prevented surface thrombogenicity under dynamic flow conditions.[6,9] In our previous study,[10] we reported that the antifouling performance of the p(HPMA) brushes increased with increasing grafting density of the polymer chains. Importantly, we showed how the selection of the grafting method directly affects the grafting density of the p(HPMA) coatings on the surface and that denser polymer brushes can be achieved by the grafting-from (GF) approach. Methods employed for GF typically rely on controlled radical polymerizations (CRP),[11,12] such as nitroxide-mediated polymerization,[13–15] atom-transfer radical polymerization (ATRP)[16–21] and reversible addition fragmentation chain-transfer (RAFT) polymerization.[22–28] In particular, surface-initiated (SI) RAFT polymerization is gaining increased attention due to its advantageous features, such as excellent monomer compatibility and lack of metal catalysts toxic to cells, which is beneficial for biomaterial applications.[29–31]

Besides the grafting density of the polymer brush, the molar mass of the polymer chains on the surface is also an important physical parameter influencing the coating's antifouling ability[32] but it is challenging to measure it directly.[33–35] The difficulty in accessing the molar mass distribution of surface-grafted polymer generated during SI polymerizations comes from the fact that its mass is extremely low, making analysis by typical methods such as size-exclusion chromatography (SEC) problematic. While some authors have assumed that the molar mass of the surface-grafted polymer is comparable with that of the polymer grown concomitantly in solution during the SI-polymerization,[36] experimental studies have demonstrated that the polymer molar mass on the surface and the solution-born polymers may be similar or differ greatly, depending on polymerization conditions.[37–39] Genzer's and Spencer's groups attributed this discrepancy to a phenomenon they termed "crowding" during SI-ATRP polymerization at high grafting density and/or with a high propagation rate.[40,41] Crowding limits mass transfer at the surface, slowing down

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4py00177j

FIGURE 1.13.2 An extract of an article in a scientific journal of a research report written by scientists. It is strictly structured with a pertinent title, names of authors, an abstract and the report, which uses the convention of: introduction, method, results, analysis, conclusion and ends with a reference list.

Access to scientific journals can be difficult as many journals require you to purchase a subscription or membership, though some are free. Figure 1.13.3 provides ideas for accessing scientific journals.

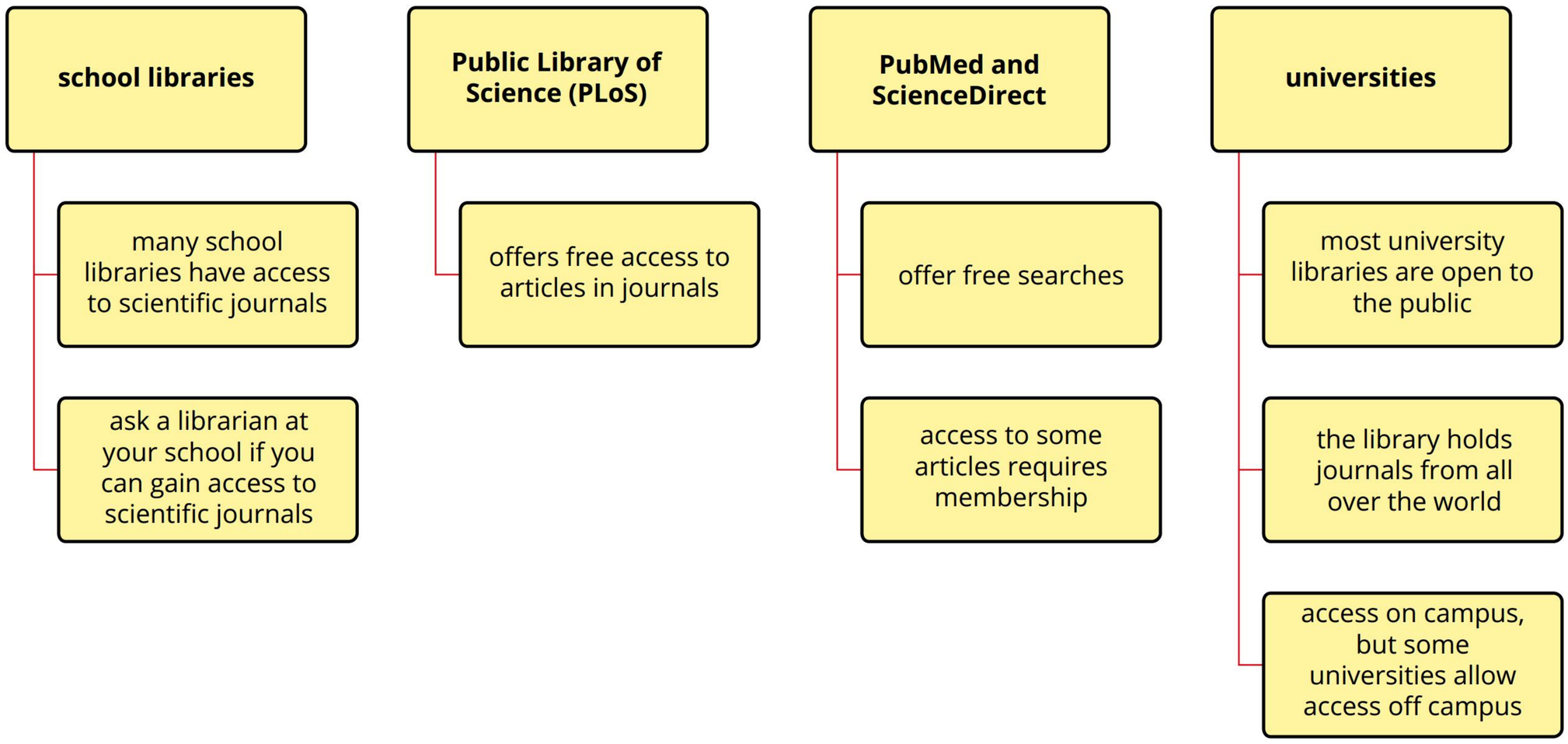


FIGURE 1.13.3 Suggestions and information on accessing scientific journal articles

Scientific articles are excellent sources of information but also have their drawbacks as sources for the research investigation. Table 1.13.4 outlines some advantages and disadvantages of sourcing and using articles in scientific journals for the research investigation.

TABLE 1.13.4 Advantages and disadvantages of scientific articles

Advantages	Disadvantages
• written by experts • authoritative information (peer-reviewed) • most current information • logical, organised layout • content is relevant to the topic • contains an abstract that summarises all information in the article (if you do not find the information in the abstract, the article is not relevant) • primary source • provides introductory comments that review the literature of the field and position of the research focus of the article in it	• information is complex and challenging to understand • uses complex language and advanced processing and analysis of data • requires a high level of scientific literacy, language and numeracy to understand • may be time consuming to read and analyse • well-established concepts do not have recent published articles • may be difficult to locate

Books and physical publications

Secondary sources such as good science magazines and books are valuable sources of secondary information.

The first source you should use is your student book. The language and concepts are presented specifically for high school students. In addition, the student book addresses the syllabus objectives. Non-fiction books and magazines will probably be commonly used resources for the research investigation. Common commercial science magazines you might find in your school library include *Cosmos*, *Scientific American* and *New Scientist* (Figure 1.13.4). Table 1.13.5 outlines some advantages and disadvantages of non-fiction books as sources for your research.

FIGURE 1.13.4 A science magazine you might find in your school library

TABLE 1.13.5 Advantages and disadvantages of book resources

Advantages	Disadvantages
• may be written by experts • potentially authoritative information • logical, organised layout • content is relevant to the topic • contain table of contents and index to help find relevant information • easily located in libraries • written in language that is understandable	• may not have been published recently • usable by only one person at a time • may have more bias than peer-reviewed papers

Searching online

Online sources include online scientific organisations such as CSIRO, NCBI, AIMS, Bioscience (Oxford Academic) and other university publications and press. Many government and privately funded science organisations publish material, along with not-for-profit scientific organisations. Websites may direct you to magazines and scientific journals (such as those described above), news, podcasts, blogs and videos (institutional, company and personal).

Information located on the internet requires very careful scrutiny. The openness and ease of publishing on the internet means information may not be valid and reliable. Use the earlier guidelines to help you evaluate sources. Table 1.13.6 outlines advantages and disadvantages of locating and using information online.

When searching for relevant information, you need appropriate search terms to enter into a search engine. These tips can help your search.

- Break your search statement into concepts and key words.
- Find synonyms, other related terms and concepts that apply to the topic.
- Create concepts of 1–3 words to enter into the search engine.
- Try different combinations of terms.
- Do not settle for the first sites on the list or your first attempt—look beyond the first page of results.
- Look through the results for sites from science organisations and research institutions (e.g. CSIRO, WEHI, NIH; .gov, .org), universities (.edu) and science journals and magazines.

TABLE 1.13.6 Advantages and disadvantages of internet resources

Advantages	Disadvantages
• quick and easy to access • allows access to hard-to-find information • gives access to the whole world; millions of websites • information is potentially more up-to-date • may be interactive and use animations to enhance understanding	• may not be reliable, valid or credible • can easily side track with non-relevant information • a lot of 'junk' sites and potentially more-biased material • need to discern search engine results to find most useful sites • cannot always tell how up-to-date information is • can be hard to tell who has responsibility for authorship • information may not be well ordered

Overview of resources

Your textbook should be your first source of reliable information. Other information should be consistent with this. Articles published in journals and magazines often present findings of new research, which may or may not be confirmed later, so be careful not to treat such sources of information as established fact. Scientific journals are **peer-reviewed** (critically reviewed by other specialist scientists), which gives them more credibility than other sources.

However, it is important that the sources utilised in the investigations are credible and easily accessible.

FORMING A QUESTION

The claim is used to develop the research question investigated in the assessment. The variables inferred from the claim may not be measurable or directly observable, and therefore they may not be scientific.

To help to develop the research question, break the claim into possible scientific elements, each of which could be used to form a question (Table 1.13.7 on page e106). Separating the claim into elements, such as related terms and concepts, enables you to formulate variables, measurable items and questions. Thus, you can identify scientific elements of the claim that are contained in the syllabus.

Based on these elements, formulate a number of questions related to the claim and record all of them in the journal. The research question must specify a dependent variable and enable a response that will evaluate the validity or the reliability of the claim. You will need to understand the dependent and independent variables and the relationship between the variables. The research question must identify the dependent variable and may also specify the independent variable.

Some guidelines to help form a research question include:

- identifying a dependent variable that can be linked to the claim or rephrasing the claim into something measurable
- developing an element of the claim into the independent variable or identifying it in the stimulus material
- phrasing a question to ask if the independent variable will influence, cause or correlate with the dependent variable
- writing a few different questions.

Usually, the questions improve as you write more, which allows the formulation of a more developed research question. At this stage, these questions can still be quite broad, but they will need to be refined; the focus of the research question needs to be very narrow so that the research report can be completed within the assessment conditions.

The process to developing a research question is often cyclical (Figure 1.13.5).

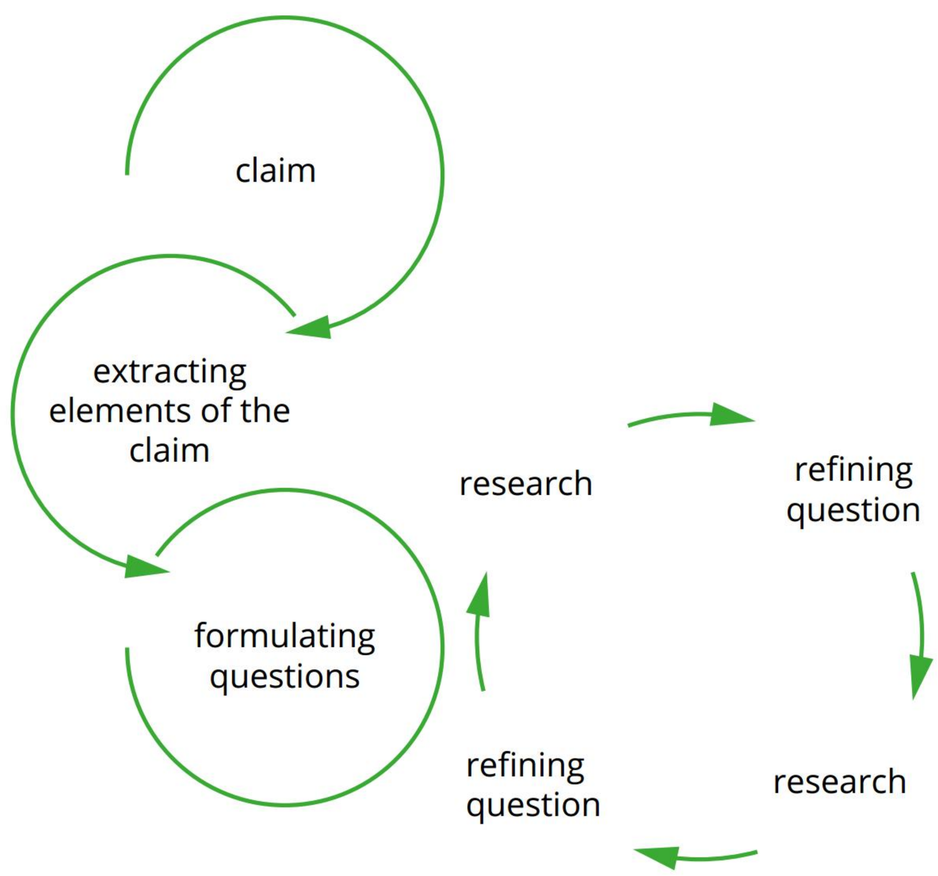


FIGURE 1.13.5 A chart of a common process for developing a research question. This cycle can be repeated as many times as necessary until a scientist is satisfied with the investigation question.

Read through Table 1.13.7 to see examples of questions formed from the elements of the claims that are refined.

TABLE 1.13.7 Three examples of questions formulated from a claim

Example claim 1: Plastics are bad for the environment.		
Elements	**Elaboration of the claim**	**Formulated questions**
Plastics are made from crude oil.	About 4% of the world's crude oil is used to make plastic.	Can the efficiency of the distillation process be increased?
	Hydrocarbons are collected by distillation.	
	Non-renewable nature of the resource.	Can the reactants in the plastics process be made from something other than crude oil?

Example claim 2: Natural shampoos are better than commercial shampoos.		
Elements	**Elaboration of the claim**	**Formulated questions**
Natural shampoos clean as effectively as commercial shampoos.	Shampoo effectiveness can be evaluated by comparing the surfactant properties of the shampoos.	Does a greater reduction in the surface tension mean that the shampoo is more effective?
	Surfactants have a non-polar aliphatic chain and polar head.	Do natural shampoos work in the same way as synthetic shampoos?
	Properties: • surface tension • wetting ability • solid content • detergency • foaming ability	

Example claim 3: Green chemistry is clean chemistry.		
Elements	**Elaboration of the claim**	**Formulated questions**
Green chemistry is a more efficient process than other methods.	Atom economy can be compared for various processes to measure efficiency.	Can the chemical yield of a reaction be increased?
		Does a higher atom economy mean a greener product?
		Is it possible to make the same product in different ways?

REFINING THE RESEARCH QUESTION

One of the questions in your journal will become your research question. As you conduct research into the independent and dependent variables, new information will refine the question, making it more specific.

Since the Forming and finding criterion assesses the development of the research question from the claim, it is important to record your development of conceptual understanding and the knowledge you gain about the relationships between variables.

Table 1.13.8 compares a formulated question with a developed research question. Always get the teacher to assess your research question.

TABLE 1.13.8 Development of the original questions formulated into research questions

Example claim 1: Plastics are bad for the environment.		
Formulated question	**Refined research question**	**Variables**
Can the efficiency of the distillation process be increased?	If the number of stages within the fractional distillation tower is increased to collect fractions with a smaller temperature range, could polymers be made more environmentally friendly?	*Dependent:* Carbon footprint of the resulting polymers *Independent:* Number of stages in the distillation tower **OR** fraction size
Can reactants in the plastic process be made from something other than crude oil?	Can the monomers that are used to generate the plastics used in polyurethanes be generated from a renewable resource?	*Dependent:* Number of monomers *Independent:* Renewable resource

Example claim 2: Natural shampoos are better than commercial shampoos.		
Formulated question	**Refined research question**	**Variables**
Does a greater reduction in the surface tension mean that the shampoo is more effective?	Are natural shampoos better cleaners than synthetic shampoos based on the surface tension, wetting ability, solid content, detergency and foaming ability?	*Dependent:* Cleaning efficiency *Independent:* Shampoo type (natural/synthetic)
Do natural shampoos work in the same way as synthetic shampoos?	Do the chemicals in natural shampoos create micelles that have a non-polar aliphatic chain with a polar head that increase the solubility of the oily substances in water?	*Dependent:* Solubility of [choose a substance] *Independent:* Shampoo type (natural/synthetic)

Example claim 3: Green chemistry is clean chemistry.		
Formulated question	**Refined research question**	**Variables**
Can the chemical yield of a reaction be increased?	Would increasing the temperature in the Haber process to shift the equilibrium towards the products increase the overall greenness of the ammonia production process?	*Dependent:* Greenness of the Haber process *Independent:* Temperature
Does a higher atom economy mean a greener product?	Can improving the chemical yield of the synthetic reactions through higher atom economy create a greener manufacturing process?	*Dependent:* 'Greener' manufacturing process **OR** chemical yield *Independent:* Atom economy
Is it possible to make the same product in different ways?	Can the polymers be made from non-petroleum sources to reduce the greenhouse gas emissions associated with petroleum production?	*Dependent:* The greenhouse gas emissions associated with plastic production *Independent:* Whether the polymers are made from non-petroleum sources

Your research investigation report requires a considered rationale for the research question, displaying its clear development from the claim. Outline this step-by-step development, justifying the steps using scientific concepts, knowledge and understanding.

Therefore, a research question must explicitly identify the dependent and independent variables. The research question must be connected to the considered rationale and the topic of study.

PUTTING IT ALL TOGETHER

The structure of the research report is not mandated by the assessment specifications but needs to be presented using appropriate report conventions, such as appropriate headings and language, and sources of information need to be acknowledged using referencing conventions.

Possible report structures include headings such as Claim, Rationale, Research question, Introduction or Background, Analysis and interpretation, Conclusion and Evaluation, or organised under the headings of the ISMG criteria as stated in the Chemistry syllabus; Forming and finding, Analysing, Interpreting and Evaluating. However, you may elect to organise your report in a different but logical order.

As stated at the beginning of this module, the characteristics of the highest performance level indicate appropriate use of genre conventions and acknowledgement of sources of information through appropriate use of referencing conventions. Therefore, the report needs to follow the advice and directions presented in Module 1.8 from Part A.

The sample research investigation report that follows covers the ISMG criteria and may be used as a reference tool. Use this as a model for reference.

Forming and finding

Claim

Biofuels are more efficient and have less environmental impact than fossil fuels.

Rationale

Climate change represents a considerable challenge of our era. Projections indicate that by 2100 the Earth's average temperature could increase by between 1.5 and 4°C (IPCC, 2014). This is consistent with other atmospheric circulation models and is primarily due to the rise in CO_2, a known greenhouse gas, from fossil fuel combustion (Figure 1, NASA, 2024) (United Nations, n.d.). The combustion of fossil fuels makes up 90% of all CO_2 emissions. Biofuels, produced from plants, also produce CO_2, but as they are derived from photosynthesis, they are more carbon neutral.

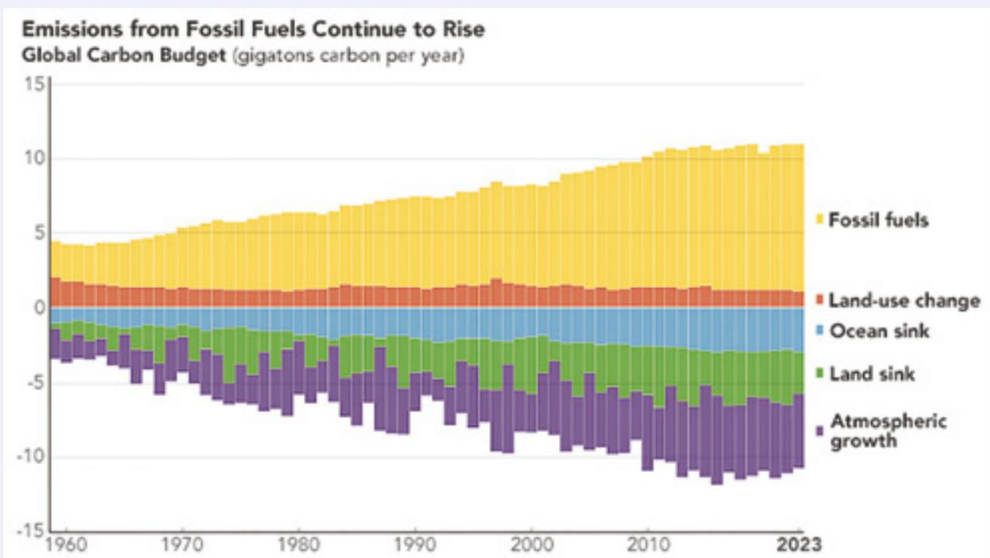


FIGURE 1 Global carbon budget (gigatons carbon per year)

General combustion reactions of fuels, shown below, are exothermic. In addition to heat, these reactions can produce carbon dioxide, carbon monoxide and water.

Complete combustion of fuels:

fuel + oxygen → carbon dioxide + water + heat

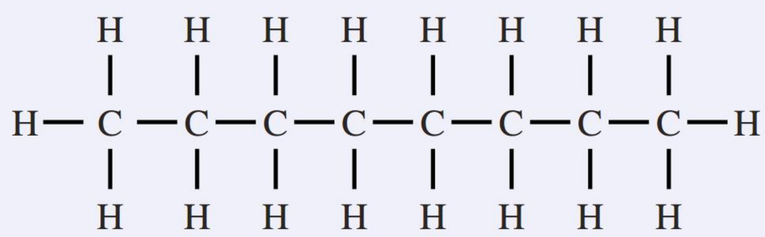
Incomplete combustion of fuels:

fuel + oxygen → carbon dioxide + carbon monoxide + water + heat

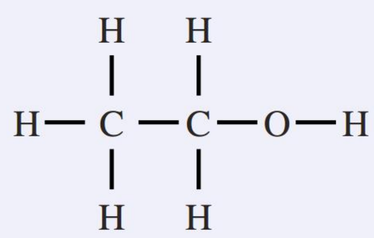
In the claim, efficiency in fuel usage encompasses a broad spectrum of terms, including complete and incomplete combustion and energy generation. Environmental impact could relate to gases produced during fuel combustion, including CO_2 (Donev, 2024), or energy and resources used (production, transport and use) and possible land use or degradation.

Fossil fuels, such as oil, are formed from decomposition of plants and animals, deep within the Earth (National Geographic, 2024). Crude oil is distilled to a range of hydrocarbons that collectively make up fuels used in transportation. On the other hand, biofuels are renewable alternatives produced by fermenting sugars from sustainable sources such as sugar cane (Queensland Government, 2024).

This study compares petrol (primarily octane) with ethanol; the structures of these compounds are shown in Figure 2.



Petrol (octane)



Ethanol

FIGURE 2 Structures of octane (found in petrol) and ethanol (bioethanol)

Petrol (gasoline) and bioethanol are examples of fossil fuels and biofuels, respectively, with ethanol already widely used as a 10% petrol additive (Wang et al., 2015) in Australia but higher proportions in fuels overseas. Due to the importance of replacing fossil fuels with biofuels, these two fuel types will be compared based on CO_2 emissions during combustion (see reactions below) and water used in their production.

The complete combustion equations for octane and ethanol:

octane: $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$
$\Delta H = -5470\,kJ\,mol^{-1}$

ethanol: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$
$\Delta H = -1360\,kJ\,mol^{-1}$

Research question

Does bioethanol have less environmental impact, with regards to lower CO_2 emissions during combustion and lower water consumption during production and use, compared to petrol (octane)?

1.14 Analysing

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- identify the variables in the research question
- determine the evidence required to evaluate the validity of the research question
- identify relevant patterns and trends in the data
- explain the patterns between the two variables
- identify the limitations or gaps that exist in evidence.

The ISMG for the Analysing criterion, shown in Table 1.14.1, is assessed in relation to the identification of just enough data that enables the research question to be answered and the identification of the limitations of the sources of the data.

TABLE 1.14.1 The performance characteristics associated with the highest performance level of the Analysing criterion

Criteria	Assessment objectives	Performance characteristics	Marks
Analysing	3. Analyse research data about the properties and structure of organic materials or chemical synthesis and design.	• the identification of sufficient and relevant evidence • thorough identification of relevant trends/patterns/relationships in evidence • thorough and appropriate identification of limitations of evidence	5

There are three aspects to the Analysing criterion.

To achieve the highest mark (5) in the Analysing criterion, you need to identify sufficient and relevant evidence to analyse the data and identify trends or patterns in the evidence. Finally, you need to identify the limitations of the evidence.

ANALYSING EVIDENCE

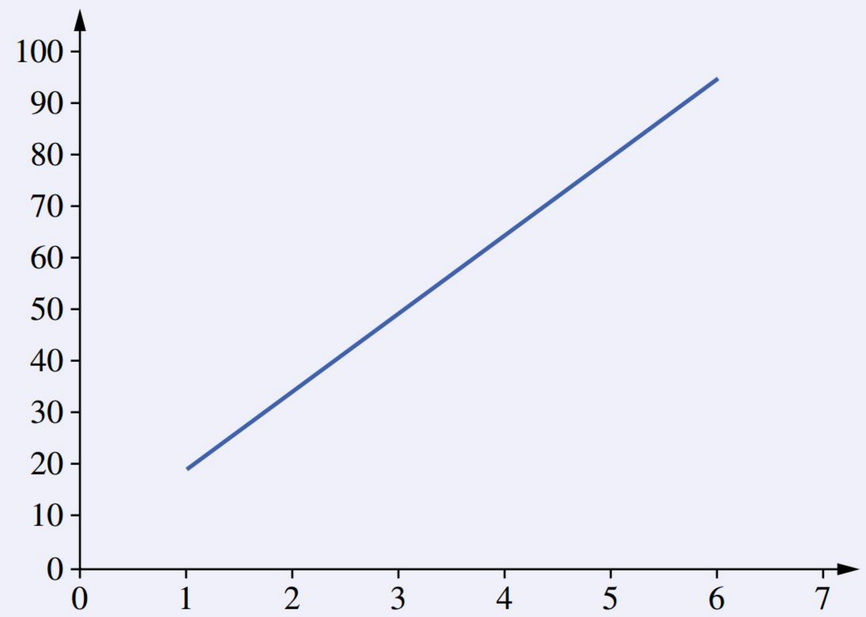
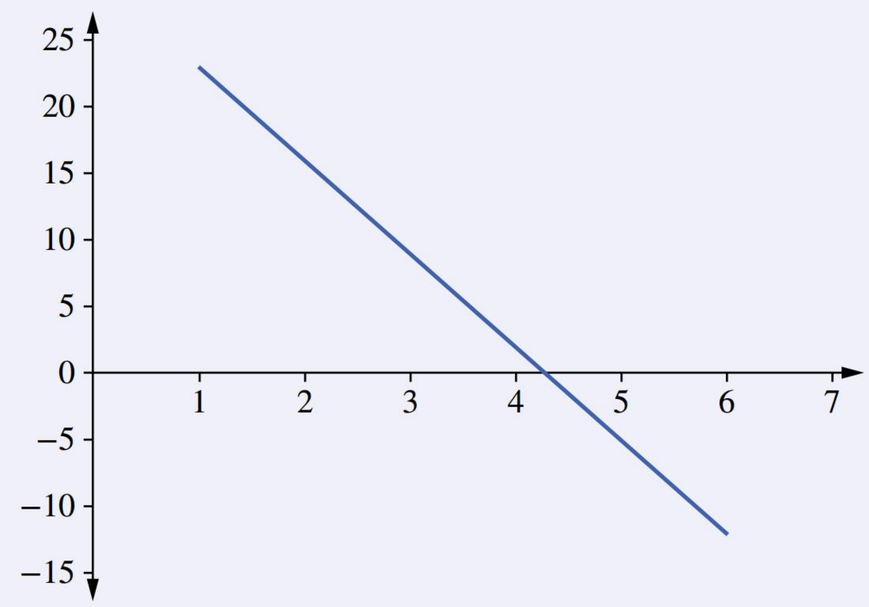
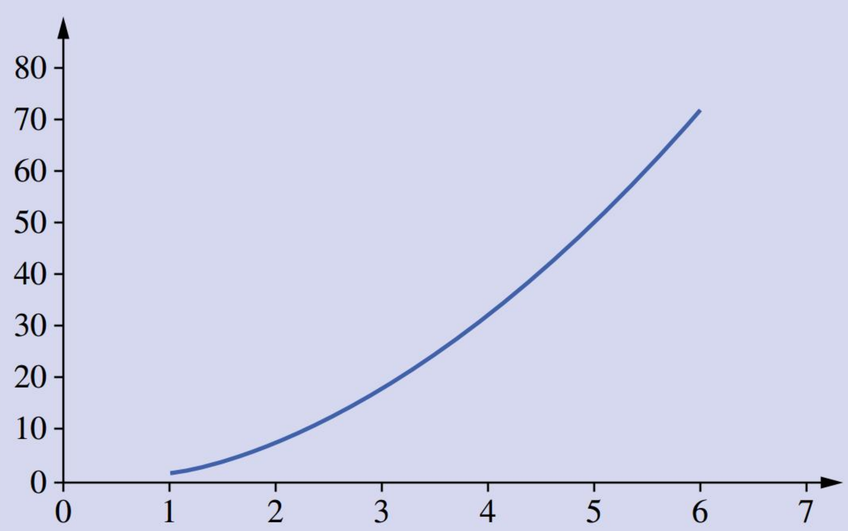
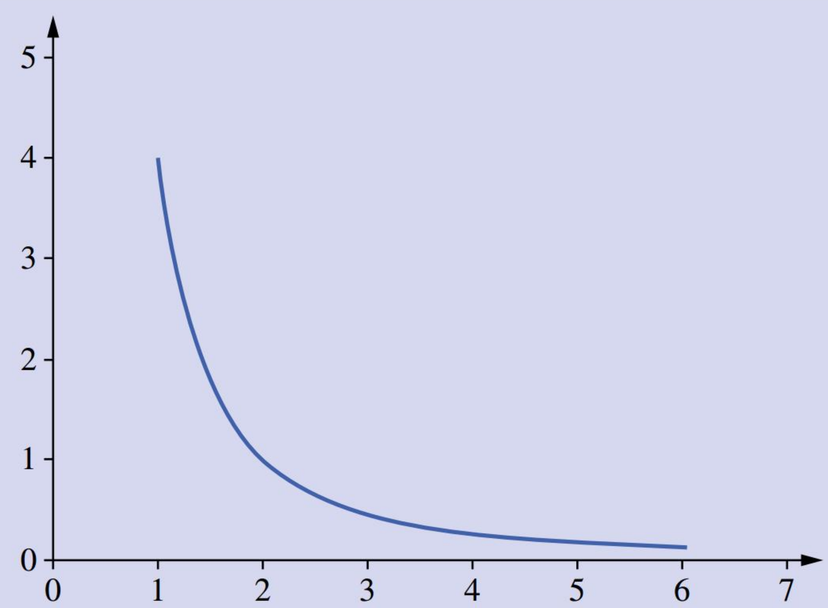
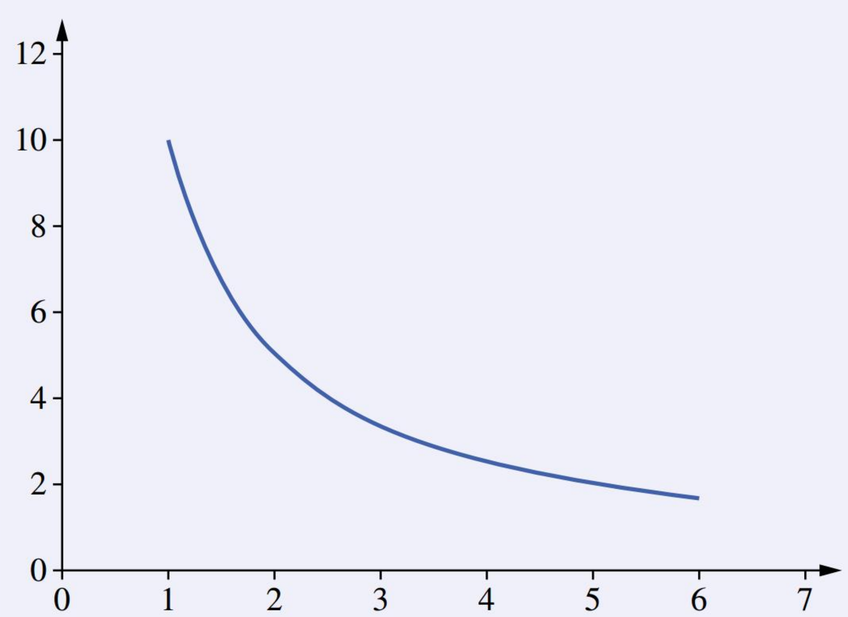
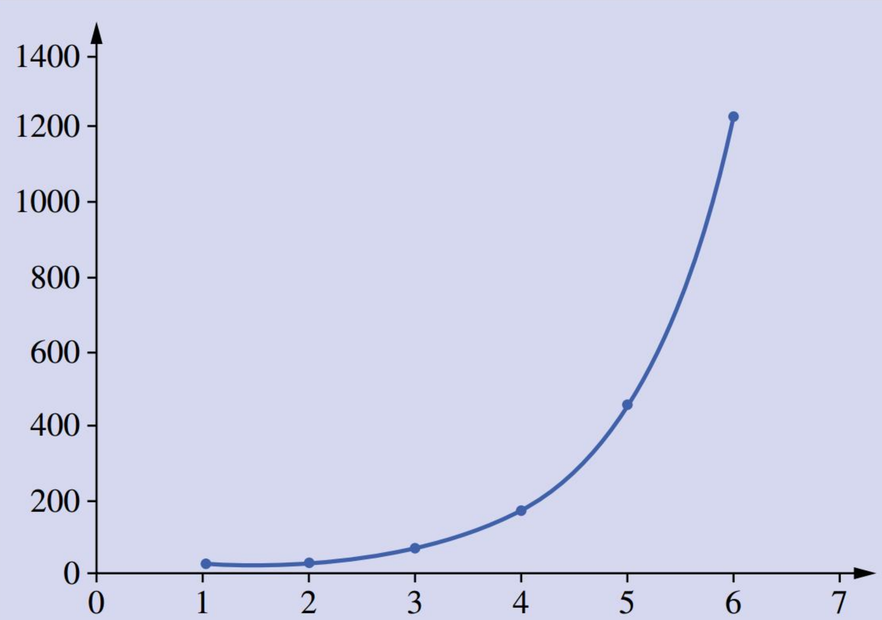
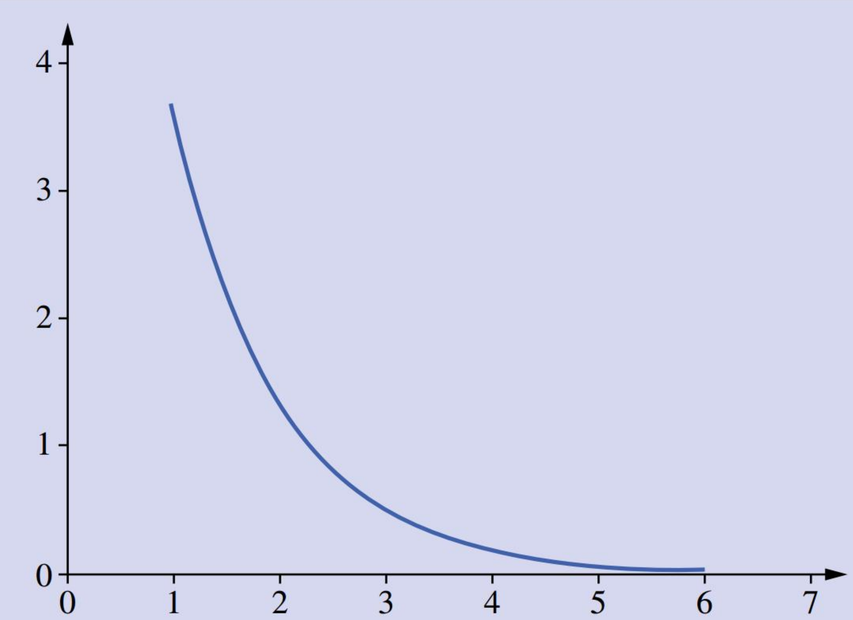
A trend or pattern is the general change in one characteristic with respect to another. In science, these are generally represented in the form of a graph with the dependent variable on the *y*-axis and the independent variable on the *x*-axis.

The first thing to notice about the trend is the shape of the graph. If there is a relationship between two variables, the trends can typically be categorised into one of five categories; linear, power, inverse, exponential and logarithmic.

In addition to the type of relationship, there are other factors to describe. For instance, does the dependent variable increase as the independent variable increases? Does the increase get bigger, as is the case with an exponential growth or does it plateau, consistent with a logarithmic change? Another way to describe a data set is by calculating the percentage difference. For example, when comparing the degree of biodegradability of two plastics over a 28-day period, this method can help quantify the relative differences. It is also important to consider that data may be presented from more than one source. The overall trend should be identified by comparing and synthesising findings from several authors to ensure a comprehensive understanding of the relationship.

Examples of the different shapes for graphical relationships are shown in Table 1.14.2.

TABLE 1.14.2 Examples of different graphical relationships: linear and non-linear (power, inverse, exponential, logarithmic)

Type of graph	Examples
Linear	 
Power	 
Inverse	
Exponential	 

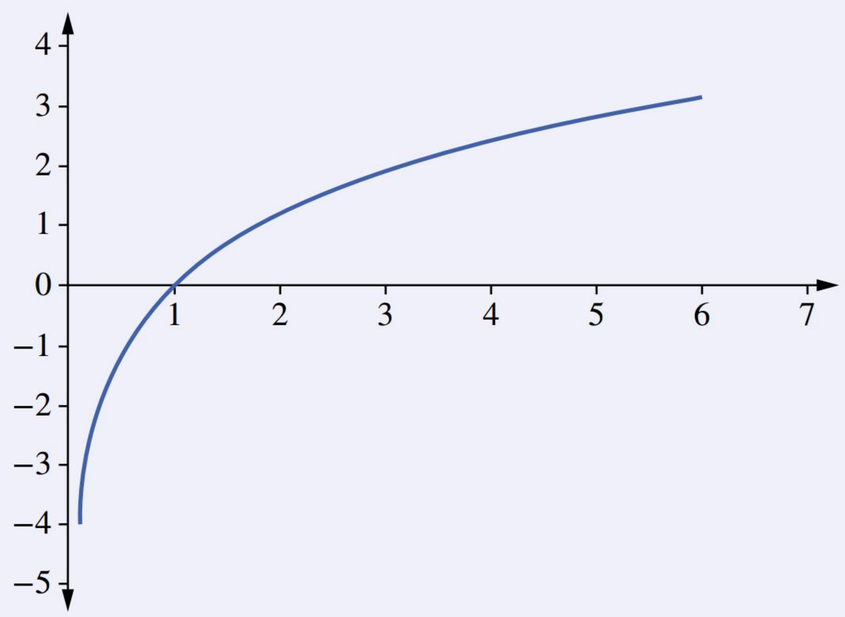
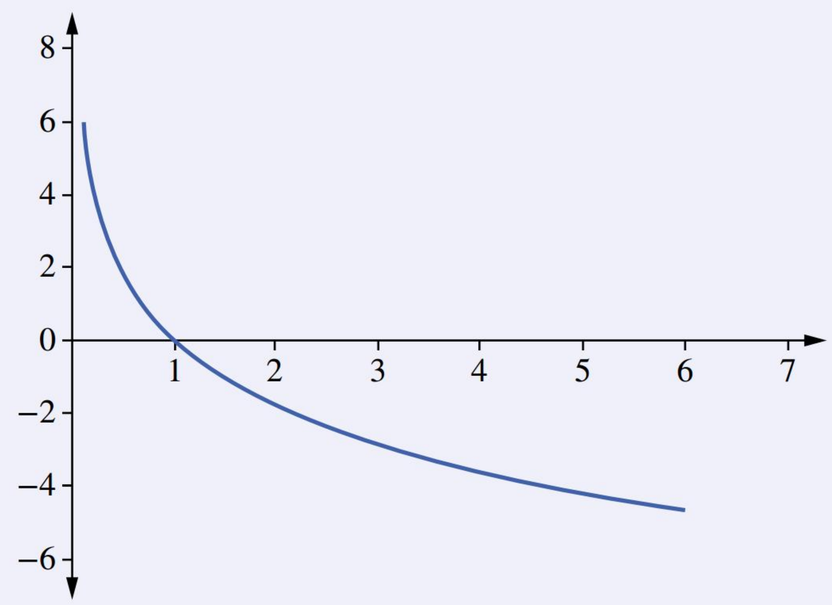
Type of graph	Examples
Logarithmic	 

Figure 1.14.1 shows a comparison of two linear trends. The graph shows the change in the mass of product as a function of time. While a trendline for each is shown, no error bars are included for this discussion. When analysing relationships, it can be necessary to compare the effects of changing conditions on the dependent variable. In addition to determining the gradients of the curves, key features such as the *x*- and *y*-intercepts are important. While both linear graphs show that as time increases, the mass of the product also increases, but the rate of increase or gradient is greater for the dashed line. The dashed line passes through the origin, while the solid line extrapolates at a negative intercept.

Note that the analysis criterion requires you to identify the relationship but not the reasons for the relationship. That will be assessed in the Interpreting criterion.

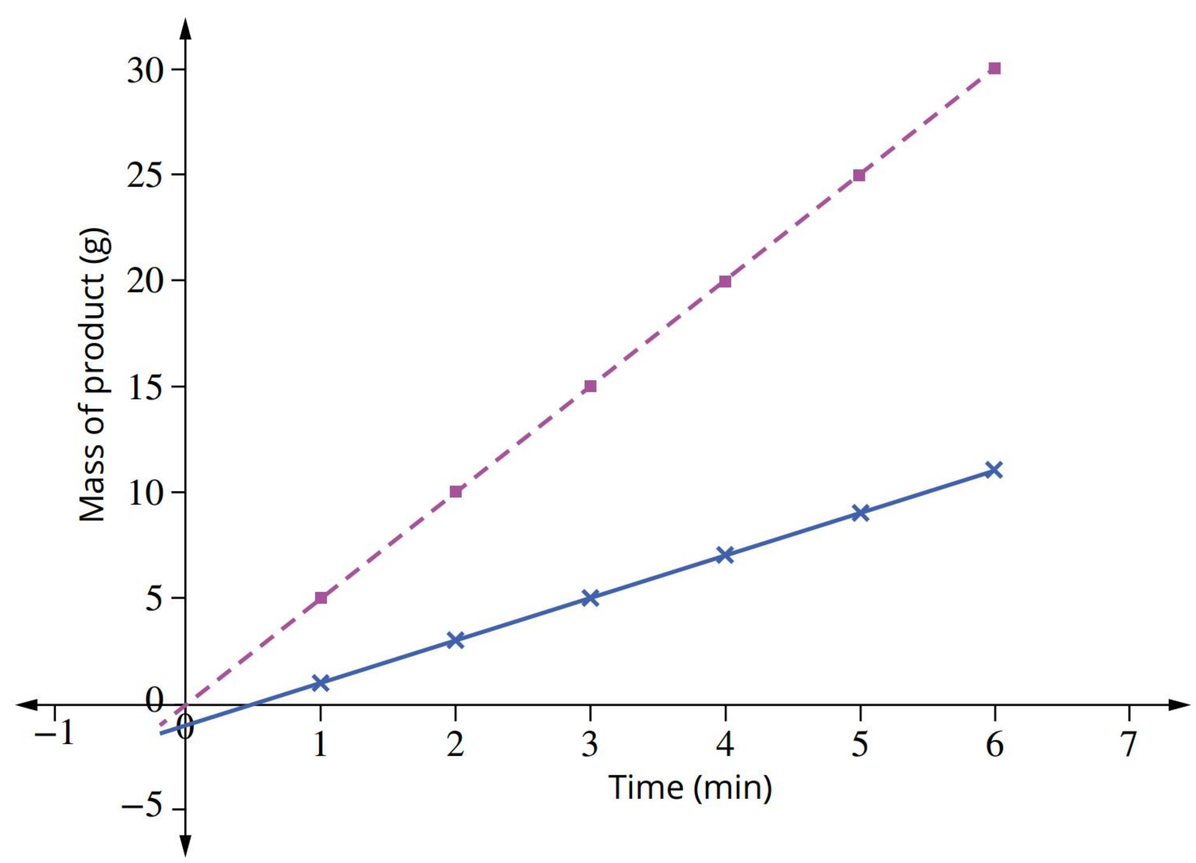


FIGURE 1.14.1 Comparison of the formation of product of a reaction under different conditions

LIMITATIONS OF THE DATA

All studies are affected by limitations. So, when analysing the data, it is important to identify the limitations. Limitations can often be grouped into three categories:

- Elements of the methodology
- Study design that impacts the interpretation of the research results
- Differences between the studies or sources used to investigate the relationship

Examples of common methodological issues include:

- selection of samples.

  Selection bias can occur if the sampling method results in the selection of samples that do not reflect the general population or population concerned.
- insufficient sample size for statistical measurements.

  It is critical to have a sufficient sample size to draw valid conclusions. More precise results can be obtained if a larger number of samples are collected, which also enable the results to be generalised to a larger population. In contrast, if the sample size is too small, it can be difficult to identify significant relationships in the data.
- lack of previous research studies on the topic.

  If the research cited is one of a limited number into the issue, the lack of available or reliable data can make it difficult to draw firm conclusions, or make connections between studies or the findings and the real world.
- methods/instruments/techniques used to collect the data.

  While it is unlikely that the students will have experience in using many of the instruments used to collect the data, the limitations in the methodology should be outlined in the discussion section of the research paper. This could include, but is not limited to, the instruments' level of detection.

The differences between the studies or sources used to investigate the relationship represent a possible third category. While they may have the same dependent and independent variables, they are unlikely to have used exactly the same methods or materials. Additionally, even if studies elucidate the same relationship between variables, they may show differences in the degree or extent of the relationship. For example, biodiesel may be shown to have lower energy content than diesel, but different studies might use oils from various plant sources or test waste cooking oil as a fuel, which may affect the results.

When reading the research papers, refer to the information about the collection of sufficient and relevant raw data in Part B on page e82. This will help evaluate the analysis of the data and identify limitations of the methodology.

As with identification of the trends and patterns, the analysis criterion only assesses the identification of the limitations of the research. The role these limitations played in the data collected and their potential impact on the study, including the inability to generalise the research findings, will form part of the Evaluating criterion.

Furthermore, the report should discuss possible ways to overcome the limitations in future studies, such as alternative methodologies and ways to avoid issues.

Ways to discuss the limitations

When identifying the limitations of the study, there are ways to introduce the discussion on the limitations.

- Possible limitations of the study include…
- The first is the… The second limitation concerns the…
- The empirical results reported by…should be considered in the light of some limitations.
- This research is subject to several limitations.
- The primary limitation to the application of these results is…
- The design of the current study is subject to limitations.
- The major limitations in this study that could be addressed in future research are first, the study focused on…Second…

Having data sources that have used different testing methods or materials can create limitations in the ability to answer the research question. For example, a catalyst shown to promote a reaction and increase yield might be studied under different reaction conditions or temperatures in different sources. Note that you will be using data from a number of sources to determine the overall trend, and it is unlikely that these researchers used exactly the same methods or materials.

SUFFICIENT AND RELEVANT

Similarly, when deciding whether the sources are relevant or sufficient, refer to Module 1.10. The analysis criterion uses the terms *sufficient* and *relevant*. However, in this case, the terms refer to the evidence. Was the data that was analysed 'enough' and 'connected with' the investigation to enable the research question to be fully answered?

PUTTING IT ALL TOGETHER

When writing the research report, it is important to evaluate the report against each criterion in the ISMG to assess the quality of the response. The analysis criterion is focused on the evidence that is collected and identifying and describing patterns or trends that are evident and connected to the research question. Therefore, it is critical that you identify the aspects of the research question that need to be answered. This will enable the search for and selection of information related to these aspects.

Once the evidence has been found, the trends need to be identified and used to answer the research question. Remember that the analysis criterion is only assessed against identification of the patterns and identifying the limitations of the research. So, to get the highest mark, the report needs to collect and analyse enough information to answer the research question.

The sample research investigation report that follows covers the ISMG criteria and may be used as a reference tool. Use this as a model for reference.

Analysing

CO_2 emissions

Wang et al. (2015) used an engine to determine CO_2 emissions of ethanol/petrol fuel blends under different engine loads (engine temperature of 80°C and speed of 2000 rpm). The study compared three fuels: pure gasoline (E0), 10% ethanol with gasoline (E10) and 10% ethanol with gasoline and water (E10W).

Figure 3 shows both E10 fuels emit less CO_2 (about 5%) compared to pure gasoline (8%) at 5 N m. When engine load increased to 60 N m, all fuels had similar CO_2 emissions between 13% and 15%.

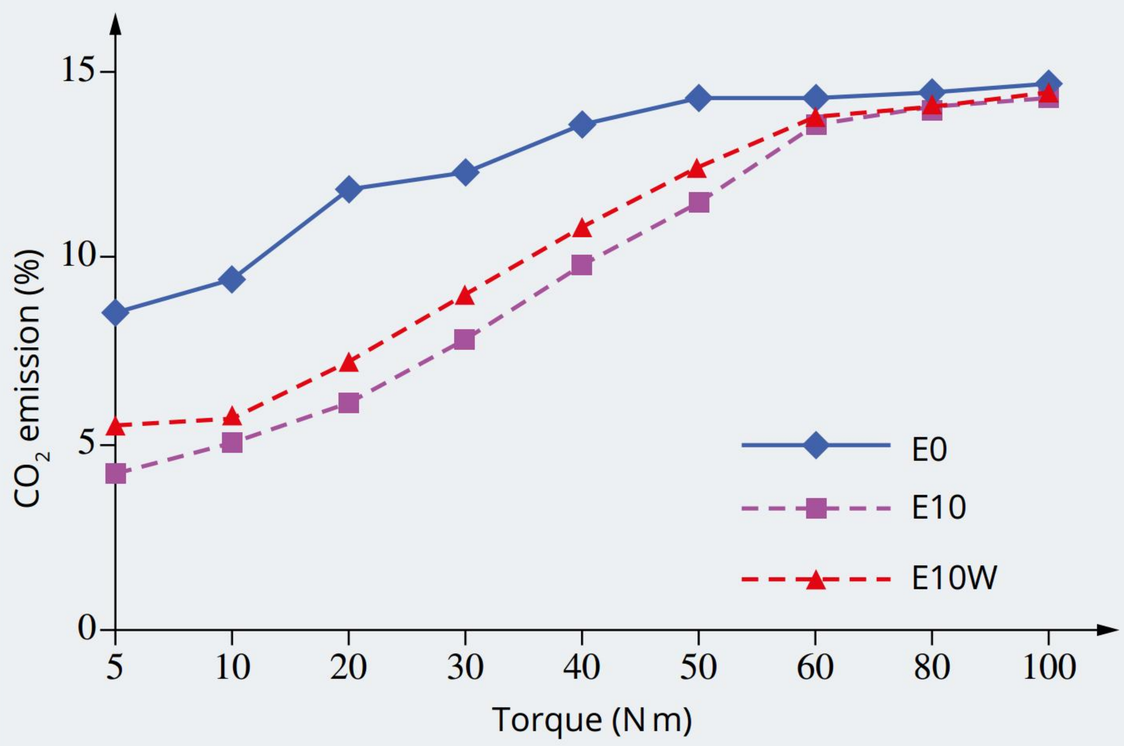


FIGURE 3 A comparison of CO_2 emissions for petrol blends at various loads

The increases in emission for each fuel are relatively linear, although the gradient for pure gasoline is less, and plateau above 60 N m.

This is consistent with tailpipe emissions reported by Natural Resources Canada (2014), which decreased from 2.29 to 1.61 kg L^{-1} as the percentage of ethanol increased.

Limitations

Wang's study (Wang et al., 2015) was conducted in the laboratory using a single engine type, with each test conducted only twice with the two results averaged. However, no information was provided about the variability of each measurement.

Values reported in the factsheet from Natural Resources Canada (2014) are estimates based on numerous factors from Environment Canada and report a single value despite emissions varying as a function of fuel density and composition.

TABLE 1 Comparison of CO_2 emissions of different fuels

Fuel	CO_2 tailpipe emissions (kg L^{-1})
gasoline	2.29
E10 (10% ethanol/90% gasoline)	2.21
E85 (85% ethanol/15% gasoline)	1.61

Water use

Lampert et al. (2016) modelled water consumption associated with production, transport and use of various fuels. Figure 4 shows that gasoline has a much lower reliance on water than ethanol (166 L GJ^{-1} versus 1933 L GJ^{-1}, respectively), consistent with Wu et al. (2009), who showed that up to 6.6 L of water was required for each litre of gasoline produced compared to 324 L of water per L of ethanol produced.

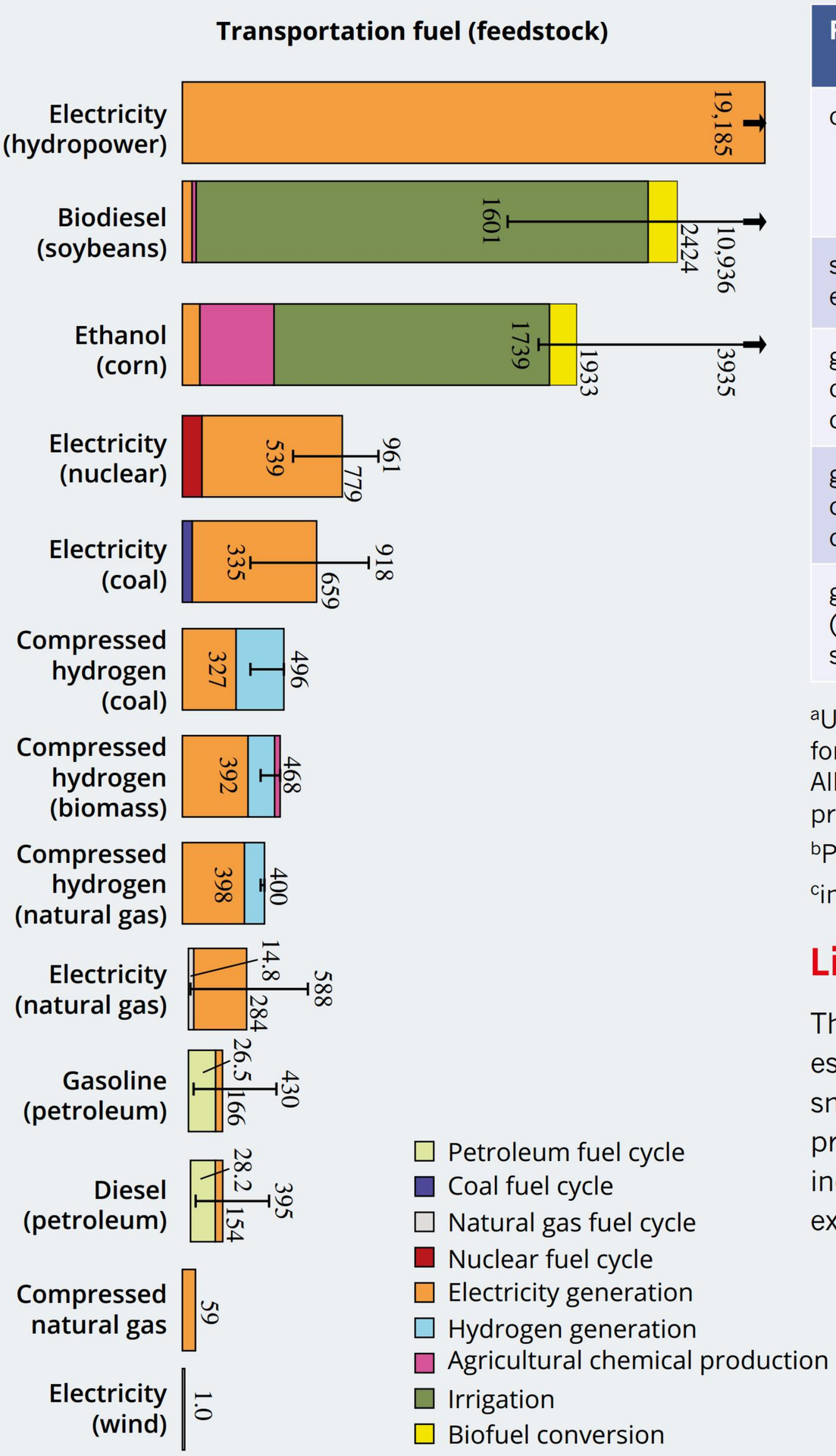


FIGURE 4 Water consumption (L GJ^{-1}) in production, transport and use of various fuels

Water used during fuel production (Table 2) included volume of water used for irrigation, excluding precipitation, and transportation. Corn ethanol has a large variation in water requirements, ranging from 10 to 324 L per L of ethanol, due to regional variation in climate and soil, compared to gasoline that has a water usage of 3.4 to 6.6 L per L of gasoline.

TABLE 2 Water consumption in the production of ethanol and petroleum gasoline

Fuel (feedstock)	Net water consumed	Major factors affecting water use
corn ethanol	10–324 L/L ethanol[a]	regional variation caused by irrigation requirements due to climate and soil types
switchgrass ethanol	1.9–9.8 L/L ethanol[a]	production technology
gasoline (U.S. conventional crude)[b]	3.4–6.6 L/L gasoline	age of oil well, production technology, degree of produced water recycle
gasoline (Saudi conventional crude)	2.8–5.8 L/L gasoline	same as above
gasoline (Canadian oil sands)[c]	2.6–6.2 L/L gasoline	geologic formation, production technology

[a]USDA regions 5, 6 and 7 combined for corn. Water consumption for corn, switchgrass and forest wood farming includes irrigation. All water used in ethanol conversion is allocated to the ethanol product

[b]PADD II, III and V combined

[c]including thermal recovery, upgrading and refining

Limitations

The error bars (shown in Figure 4 and Table 2) in estimating water consumption in fossil fuel use are much smaller than those associated with natural sources as the production of crops is heavily dependent on many factors, including irrigation, soil type and natural rainfall, which is excluded from the study.

1.15 Interpreting

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- evaluate the research process
- understand the steps and requirements for a justified argument
- identify the steps necessary to develop a justifiable conclusion.

The ISMG for the Interpreting criterion, shown in Table 1.15.1, is assessed in relation to creating scientific arguments and a conclusion, and the use of scientific language to address the research question.

TABLE 1.15.1 The performance characteristics associated with the highest performance level of the Interpreting criterion

Criteria	Assessment objectives	Performance characteristics	Marks
Interpreting	1. Describe ideas and findings about the properties and structure of organic materials or chemical synthesis and design.	• justified scientific argument/s • justified conclusion linked to the research question • fluent and concise use of scientific language/ representations	5
	4. Interpret research evidence about the properties and structure of organic materials or chemical synthesis and design.		

There are three aspects to the Interpreting criterion.

To achieve the highest mark (5) in the Interpreting criterion, you need to create justified scientific arguments and a justified conclusion to answer the research question, and present the results in the form of a scientific report using fluent language and representations.

JUSTIFYING AN ARGUMENT

When constructing a scientific argument, the claim, the evidence and the scientific reasoning need to be considered.

- The claim is what is known.
- The evidence is how this is known.
- The scientific reasoning is why the evidence supports or refutes the claim.

The QCAA glossary of cognitive verbs defines justify as 'to give reasons or evidence to support an answer, response or conclusion; show or prove how an argument, statement or conclusion is right or reasonable'.

A scientific argument is a statement, supported by multiple pieces of evidence, that is measured or observed. The argument links the evidence and reasoning together with scientific facts and knowledge. It is important to recognise that the argument could either corroborate the claim or provide evidence that refutes the claim.

Therefore, the investigation needs to use the information and evidence collected from the research to answer the research question rather than simply opinions or beliefs that cannot be empirically verified.

The Introduction outlined terms and concepts related to the topic, which were used to develop the research question. This helped identify variables linked to the research question to be analysed. Then, the Analysis section of the report identified patterns and trends in the data related to the research topic.

The Interpretation section of the report needs to explain the trends between the variables to explain the research question.

Common things to avoid

When writing the justification, it is important to be concise and to the point. Select data and explain how the evidence is linked to the research question. Ignore evidence that has no relevance to the research question.

Be selective about the information discussed. The specifications of the assessment task state that the length of the report is limited to 2000 words. The justification needs to emphasise the significance of the research to the research question or topic. How do the trends identified in the Analysis section support the conclusion that was drawn? If the data does not directly address the question, it should be removed from the report. It is not necessary to use the whole of the data from the research; only use parts of the data that address the research question.

DRAWING A CONCLUSION

When writing the conclusion, make sure that it explicitly answers the research question. The easiest way to do this is to state the research question and summarise how the evidence supports the research question in about 150 words. In the summary, refer to the key evidence and authors or figures. In addition, concisely outline key limitations and how they contradict the conclusion with respect to the research question. The conclusion usually contains the scientific argument for the dependent and independent variables relationship that has been identified.

PUTTING IT ALL TOGETHER

There is no singular way of creating a justified argument to answer the research question or write the conclusion. The interpretation of the research collected simply needs to create justified arguments that use the evidence to explain and answer the research question to form a justified conclusion.

The sample research investigation report that follows covers the ISMG criteria and may be used as a reference tool. Use this as a model for reference for justified arguments that link the research question and evidence, enabling a conclusion supported by reasoning and scientific understanding to be drawn.

Interpreting

Data show that octane generates more CO_2 per litre of fuel burned. When 1 mole of octane is burned, more energy is released compared to ethanol (NIST Chemistry Webbook), which is not surprising as octane forms more C=O and H–O bonds in carbon dioxide and water per mole.

TABLE 3 Comparison of thermodynamic data and moles of CO_2 produced as a function of energy and volume of fuel burned

Compound	Heat of combustion ($kJ\,mol^{-1}$)	Moles CO_2 produced ($mol\,kJ^{-1}$)	Moles CO_2 produced ($mol\,L^{-1}$)
ethanol	1366.3	1.46×10^{-3}	34.2
octane	5430	1.47×10^{-3}	49.2

Based on thermodynamics, CO_2 emissions for the fuels are almost identical. However, when density is taken into account, octane produces 43% more CO_2 per litre of fuel burned than ethanol (Table 3). This is consistent with observations of higher CO_2 emissions from gasoline than ethanol (Wu et al., 2016). However, since only 10% of the fuel was ethanol (E10 and E10W), this cannot account for the whole of the difference (8% compared to about 5%) at 5 Nm torque. The 43% higher emission for pure gasoline ($mol\,L^{-1}$) is of a similar magnitude to the estimate from Natural Resources Canada (2024), which reports that CO_2 emission with gasoline is about 42% higher than the 85% ethanol mix.

One limitation of this approach is that it does not take into consideration the engine efficiency, driving styles and engine age with respect to the fuels.

As engine torque increased, the difference in CO_2 emissions for the fuels decreased to become negligible above 60 N m, suggesting either a change in combustion efficiency of the engine at higher loads or that octane combustion is less complete, so carbon monoxide is produced.

While emissions appear to be higher for gasoline, the greater energy stored in octane means that the two fuels produce similar amounts of CO_2 per kJ of energy produced, so would be as environmentally harmful as each other with respect to CO_2 release.

Lambert et al. (2016) and Wu et al. (2009) both show that bioethanol production consumes varying amounts of water from 1.9 L to 324 L of water per litre of ethanol (Table 2) due to varying irrigation requirements, whereas gasoline production uses significantly less water from 2.6 L to 6.6 L to produce the same amount of fuel. This is due to the different nature of the fuels and their production. Crop cultivation (biofuel) requires water, which if not provided by the rain is reliant on extensive irrigation. The locations of the corn farms (or sugar in Australia and Brazil) across US account for the large variability in the values in the studies, as the growth of crops depends on the soil and water irrigation usage and would vary based on natural rainfall and irrigation from local water sources. Furthermore, biofuel production is a relatively new process that is less optimised and developed than the processing of crude oil, which is over 100 years old.

These two studies are limited in investigating water used in fuel production and do not take into account water use during other aspects. Additionally, the studies provide water use in different units, limiting comparison as ethanol and octane have different energy content (1366 kJ mol^{-1} and 5430 kJ mol^{-1}, respectively).

Conclusion

While 43% more CO_2 is emitted per litre for gasoline, when calibrated to the amount of energy generated, both fuels produce similar emissions of CO_2 (1.46×10^3 mol kJ^{-1}). If engines for both fuels are equally efficient, then for the same distance travelled, the same amount of CO_2 is produced. However, the production, transport and use of bioethanol requires more water as a result of irrigation required for the growth of the crops.

Therefore, the research question is disproven, as while both fuels emit the same amount of CO_2 to travel the same distance, much more water is required in the production, transportation and use of bioethanol.

1.16 Evaluating

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- evaluate the research process
- identify the steps necessary to develop a justifiable conclusion
- evaluate the quality of the evidence
- extrapolate the conclusion to the original claim.

The ISMG for the Evaluating criterion, shown in Table 1.16.1, is assessed in relation to evaluating the quality of the evidence, generalising the information to the original claim and suggesting improvements and extensions that relate to the claim.

TABLE 1.16.1 The performance characteristics associated with the highest performance level of the Evaluating criterion

Criteria	Assessment objectives	Performance characteristics	Marks
Evaluating	5. Evaluate research processes, claims and conclusions about the properties and structure of organic materials or chemical synthesis and design.	• justified discussion of the quality of evidence • extrapolation of credible findings of the research to the claim • suggested improvements and extensions to the investigation that are considered and relevant to the claim	5

To achieve the highest mark (5) in the Evaluating criterion, you need to evaluate the quality of information used to support the scientific arguments. This requires an explanation of the limitations of the data, including an assessment of the statistical quality of the data, such as R^2 value or error bars. In addition, while the focus of the report is to justify a very narrow research question, this section needs to generalise the findings to the much wider claim, i.e. if the findings were more widely applicable, how would this impact the claim? Finally, identify improvements and extensions to strengthen the findings and further justify the answer to the research question.

EVALUATE THE QUALITY OF EVIDENCE

The analysis section of the report identified limitations in the data. This section of the report needs to explain how the limitations identified in the data and the sources used to support the argument affected the ability to evaluate and answer the research question.

Questions that could be useful to answer when evaluating the reliability of the data include:

- Were the statistical measures of the data good and appropriate?

  This could be shown by an R^2 value close to 1 or very small error bars in the data trend.
- Was the sample size sufficient to say that the findings were valid?

  As the sample size increases, the standard deviation of the results decreases, meaning that the chance of results being skewed by a single outlier is less.
- Were the findings reproducible?

  The results of the research investigation were corroborated by other studies and research institutions.

  The experiments in the study were repeated with different techniques and the findings were consistent or independent of the methodology chosen, without a justifiable reason why they might vary.
- Did the result occur only under very specific conditions, and were these conditions applicable to the real-world scenario?

- Was the methodology and instrumentation able to be applied appropriately to the situation studied?
- If the study had to investigate concentrations significantly greater than those that exist in the real world, can the findings of the research be applied to the real world?
- Are the theories that the authors used to support their findings still valid?
- Do the results fit the accepted theories or equations? In Figure 1.14.1, one of the trendlines went through the origin. This means that at the start of the experiment the mass of products formed was 0 g; however, the other trendline went through –1 g. This makes no sense in relation to the experimental data, and so indicates that the results of this study may not be reliable. It is likely that these issues will have been identified and discussed by the authors in a peer-reviewed journal.

It is important not to just repeat the statements made earlier in the analysis, but to describe their effect on the investigation.

In addition to evaluating the data analysed, the investigation needs to evaluate whether the sources that were used were reliable.

EVALUATING SOURCES FOR VALIDITY AND RELIABILITY

Determining the validity and reliability of a source can be a challenging task. For some sources, it is easy to find details about the author, evidence and concurrency, while others only contain content and do not offer any other details. Another difficulty is when learning about a new topic or concept it can be challenging to tell if a source is valid or not.

Examples of questions to consider when evaluating the sources include:

- Who or what organisation commissioned the report?
- What qualifications do the authors have?
- Is the source peer-reviewed or have a bias that might influence their findings?
- Is the information provided referenced and are the sources of this information reliable?
- When was the research reported? This is important as theories and concepts can be influenced by the year in which they were published.
- Are the findings reported in the publication supported by other sources? This will be found in the introduction, where the author identifies background information and gaps in the current understanding of the topic.

Table 1.16.2 outlines an example of evaluating a resource step-by-step in relation to the research article (Figure 1.16.1) that relates to silica aerogels.

Effect of silica aerogel on thermal insulation and acoustic absorption of geopolymer foam composites: The role of aerogel particle size

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ABSTRACT

Silica aerogel features super thermal insulating and excellent sound absorption. Although the application of silica aerogel in building materials for energy saving has been investigated recently, the role of aerogel particle size on geopolymer foam render can be crucial but is rarely studied. In this research, four kinds of silica aerogel with different particle sizes (2–40 μm, 100–700 μm, 100–1200 μm, 700–4000 μm) are applied in geopolymer foam aerogel render (GFAR) to improve the thermal insulation and acoustic absorption performance. Results show that larger silica aerogel particles are more beneficial for acoustic absorption and thermal insulation while smaller aerogel particles are less effective for insulation properties. The microstructure of GFAR is investigated in-depth with micro-CT, optical microscopy and ultrasonic pulse velocity test. The mechanism of the improved performance of GFAR with different silica aerogel is explained. The optimal geopolymer foam aerogel render (GFAR) reaches a thermal conductivity of 0.133 W/(m·K), an average value of acoustic absorption coefficient of 0.51 with a density of 715.2 kg/m^3. The result of this study is essential to enlighten the use of larger silica aerogel particles in geopolymer foam render, focusing on a low dosage of silica aerogel while utilize its full benefit.

1. Introduction

The energy-saving of the building sector and the comfort of the indoor living environment have received rising attention due to the increasing awareness of sustainability and the quality of life [1]. The building industry is responsible for almost 40% of the total energy and CO_2 emission in developed countries [2]. For now, many countries have already initiated policies to decrease heat loss through building shells [3]. Moreover, the functionalization of insulation materials is also very important, for instance, improving the acoustic absorption performance to increase the quietness of the indoor environment [4,5] and reduce the noise pollution generated from daily life [6]. Therefore, developing newly high-performance insulating lightweight materials is of significant urgency.

Silica aerogel is a super-insulating inorganic material [7], consisting of a 3D network of crosslinking silica nanoparticles and 95%–99% of air [8]. Thanks to the high porosity and low solid thermal conductivity (λ), the effective thermal conductivity of silica aerogel is pretty low, normally achieving 0.012–0.018 W/(m·K) [9]. However, the silica aerogel is very brittle and easy to break, the commercial silica aerogels are always produced in a powder or particle form [10]. It is often incorporated in other matrices, like fibreglass mats or other lightweight materials to facilitate its benefits [11]. Several investigations related to the incorporation of silica aerogel in building materials have already been carried out as presented in Table 1. Ng et al. [12] prepared high-performance aerogel concrete, with bulk density and thermal conductivity of 1300 kg/m^3 and 0.4–0.5 W/(m·K), respectively. The concrete has a low water to binder ratio of 0.20–0.25 and a silica aerogel replacement ratio of 50%–70% with sand. Tao et al. [13] developed normal cement mortar with an aerogel replacement ratio of 60%, featuring a compressive strength of 8.3 MPa and thermal conductivity of 0.26 W/(m·K). Júlio et al. [14] prepared lightweight aerogel aggregate concrete with a 100% replacement ratio of silica aerogel with sand, resulting in concrete with very low thermal conductivity of 0.085 W/(m·K) but compressive strength of only 0.41 MPa. Seo et al. [15] investigated the silica aerogel used in fly ash/slag geopolymer concrete, with an aerogel concentration of 25%–75%. However, the thermal conductivity is relatively high, reaching 0.8 W/(m·K). Zhu et al. [16] investigated the cement-based mortars and coatings with the addition of silica aerogel. The thermal conductivity is low (0.17 W/(m·K)) with a

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1359-8368/© 2022 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

FIGURE 1.16.1 A peer-reviewed research article titled 'Effect of silica aerogel on thermal insulation and acoustic absorption of geopolymer foam composites: The role of aerogel particle size'.

TABLE 1.16.2 Evaluation of a resource

Source evaluated: 'Effect of silica aerogel on thermal insulation and acoustic absorption of geopolymer foam composites: The role of aerogel particle size'			
Criteria		**Decision**	**Support/justification**
primary or secondary	Is this an eyewitness account or a second-hand source?	primary	• Research article published in www.Sciencedirect.com • Research results published in article
validity	Does it contain information that is specifically related to the claim?	yes	• Outlines information directly related to the performance of aerogel as thermal insulation
	Is the evidence and information pertinent to the variables in the research question?	yes	• Information, experiment and results are specific to the performance and physiochemical properties of aerogel.
reliability	Is it current/recent information?	yes	• Published Aug 2022 • This is quite recent, but aerogels are modern materials undergoing a considerable amount of research. There may be newer information available.
	Is it up to date in its understanding of relationships?	yes	• Information outlined about thermal conductivity and properties of aerogel
	Is the evidence equivalent to other sources?	mostly	• Table 1 within the article contains a list of six similar experiments.
	Check the credibility—consider who the author is, their qualifications and expertise.	good	• Authors are from the School of Civil Engineering at Wuhan University or the Department of the Built Environment at Eindhoven University. • *Journal of Basic and Applied Sciences* is a reputable peer-reviewed journal.
	Try to find the sample size.	known	• Six samples, three trials per sample
	Try to establish what variables were controlled or measured.	known	• Methodology of the preparation, storage and testing of the samples is detailed, including controlled variables such as air temperature and humidity.

A judgement could be made about the credibility of this source, such as: 'The information and evidence was published by experts in a peer-reviewed journal article that is concurrent and with variables of experimentation known and directly related to the claim and research question. However, as the results are new, it is yet to be seen if they are substantiated, therefore affecting the reliability of the evidence. This resource is both valid and reliable.'

EXTRAPOLATION TO THE CLAIM

The first stage of this assessment involved narrowing the claim to a very specific research question. This could have meant selecting a specific material or smaller temperature or concentration range. The Extrapolating criterion requires inferring how the trends and patterns identified and explained in the earlier sections of the research report could be extended to the original claim.

When exploring the claim, the students identified the dependent and independent variables associated with the claim. Thus, questions that can help students extrapolate the findings and conclusion to the claim include:

- what are the dependent, independent and controlled variables associated with the claim?
- what is the impact on the dependent variable when the independent or controlled variables from the research question are extended to include the claim?

IMPROVEMENTS AND EXTENSIONS

Suggest improvements and extension(s) that would complement the research findings and have the potential to provide new evidence that could be used to evaluate the research question (improvements) and claim (extensions) further. These should be linked to the identified limitations (analysis and quality of evidence—make sure not to repeat yourself—can just identify the issue).

The highest achievement level requires that suggested improvements need to be considered and relevant. There are two obvious areas that could be the focus of the suggested improvements. First, a good place to start when proposing possible improvements is the limitations in the research and evidence that were identified and explored in the previous sections of the report. Second, identify what information is required to provide more definitive proof of the research question.

As discussed in the limitations, these could come from the methodology or the interpretation of the results. It could be useful to consider the following:

- changes to the method of selecting samples to reduce bias
- increasing the sample size to increase the accuracy of the results or reduce the errors associated with the measurements
- methods/instruments/techniques used to collect the data. Were the measurements below the limit of detection or so low that the associated error was large? Has technology advanced since the previous research, which means that the relationship can be more accurately determined?
- gaps in the evidence that you identified through your investigation.

These considerations could form the basis for your suggested improvements. While a detailed explanation of these is not required, the report should identify how they would benefit your investigation.

Suggestions of possible extensions to the research investigation could be identified from the information collected as part of the research investigation. Students should ask themselves if there were limits to the scope of evidence available.

- During the research, did you identify areas that could be explored further?
- Could the conclusions from your report be extended to another situation?
- When extrapolating the research question to the claim, were there any aspects that could not be proven because information was not available?

PUTTING IT ALL TOETHER

The sample research investigation report that follows covers the ISMG criteria and may be used as a reference tool. Use this as a model for reference.

Evaluating

Extrapolation to claim

While the research question is disproven, biofuels may be more efficient and have less environmental impact than fossil fuels as stated in the claim as these studies investigated only a few aspects related to environmental impact. The combustion of bioethanol releases the same amount of carbon dioxide to produce the same energy as gasoline; however, other environmental impacts such as biodegradability, land use and energy required during production have not been addressed. The efficiency (e.g. energy content) of biofuels and fossil fuels has not been investigated here, and only one biofuel and fossil fuel are investigated. As not all aspects of environmental impact nor efficiency have been researched, the claim cannot be proven.

Quality of evidence

Studies (Wang et al., 2015 and National Resources Canada, 2014) investigated the CO_2 emissions of ethanol compared to gasoline. However, Wang (2015) only investigated engine load parameter, which affects CO_2 emissions. If the load of an average passenger vehicle or transport vehicle is 60–100 N m, the difference in CO_2 production per L during combustion is negligible (Figure 3), but as a function of energy, CO_2 production is less. This limits the ability to answer the research question and claim.

Wu et al. (2009) and Lampert et al. (2016) both model water use. However, units are different—L/L or L/GJ. This is a limitation because ethanol and octane have very different energy content, 1367 kJ mol^{-1} and 5430 kJ mol^{-1}, respectively. Water use of ethanol estimated per litre will need to be multiplied by approximately 4 to estimate water use to provide the same energy as gasoline.

Furthermore, the ability to conclude from Wu et al. (2009) is limited as the source is over 10 years old and may not be relevant to current water consumptions of ethanol and petrol. However, all sources are retrieved from peer-reviewed scientific journals, indicating their reliability. Also, the National Resources Canada data are limited and uses second-hand modelling data.

Improvements and extensions

To fully determine the environmental impact of bioethanol with respect to CO_2 emissions and water consumption during production compared to petrol, further testing is required. Further studies on the production, transport and use for each fuel are required as only one author is provided.

The use of water showing bioethanol is a greater risk to the environment is complicated by the fact that technologies for ethanol production are not optimised as with crude oil and petrol, which are over 100 years old. Information is required about more up-to-date biofuel production techniques, which likely are more efficient. This means negative environmental effects of producing bioethanol may decrease and feasibility of using the fuel will increase.

More information relating to the general engine loads of vehicles using these fuels is required and carbon dioxide emitted as a function of distance travelled.

To further answer the claim, the efficiency of a larger range of biofuels compared to fossil fuels should be investigated, such as biodiesel and biogas. Furthermore, the efficiency of more engines should be investigated as Wu et al. (2015) only investigated one engine. Environmental impact can be further investigated by analysing energy related to the production and use of alternate fuels.

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PART D EXAMINATION

The examination is set externally by QCAA and covers both Units 3 and 4 of the syllabus. The examination accounts for 50% of the total assessment in chemistry and is delivered in two 90-minute papers on the same day (morning and afternoon).

The QCAA defines an examination as a supervised test that assesses the application of a range of cognitions to one or more provided items such as questions, scenarios and/or problems. Students complete their responses individually, under supervision, and within a set time.

The assessment objectives are to:

- describe ideas and findings
- apply understanding
- analyse evidence and identify trends, patterns, relationships, limitations and uncertainties in data
- interpret evidence, analyse and draw evidence-based conclusions.

The following table outlines key information about each exam paper. Look at the table carefully and make yourself familiar with the unique features of each paper.

Examination	Key information
Paper 1	multiple-choice questions (20 questions) short-answer questions consisting of: • single-word answers • sentences • paragraphs • calculating using algorithms • interpreting using graphs, tables or diagrams • responding to unseen data and/or stimulus
Paper 2	short-answer questions consisting of: • single-word answers • sentences • paragraphs • calculating using algorithms • interpreting using graphs, tables or diagrams • responding to unseen data and/or stimulus
syllabus coverage	• Units 3 and 4
conditions	• perusal (reading) time: 10 minutes • writing time: 90 minutes
equipment	• QCAA-approved graphics calculator permitted • approved writing equipment • seen formula and data booklet provided
marks	• constitutes 50% of the total assessment

Engage in positive 'self-talk'. You know more than you think you know.

Careful and thorough preparation for the examination should help reduce some of the anxiety and stress you may experience in the lead-up to this assessment. Many students feel that their performance in the examination, as in all assessments, is what will define them and determine their future career paths.

Remember, no matter how you feel about your performance, there is nothing you can do to change it. If you have not achieved the score that will gain you entrance into the course for your preferred career path, consider your options. Investigate different pathways to move towards your goal. Consider different courses. Seek advice from your teachers, especially your careers teacher. Sometimes the path to achieve a career goal is less direct, or a different career will be more suitable.

It is very common and easy for students to become 'consumed' by the demands and pressures of their final year of school. So, remind yourself that there is life beyond Year 12!

This guide provides you with practical suggestions and support to prepare for the examination. The guide takes a year-long approach to your preparation that includes:

- consolidating learning—effective learning routines and strategies for use throughout the year
- revising and practising—study practices and strategies for the weeks leading up to the examination
- sitting the exam—strategies and hints for tackling the examination
- after the exam—some considerations.

1.17 Examination preparation

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- cover all aspects of the syllabus
- focus on key concepts
- give greater emphasis to larger topics than minor ones
- include examples and applications
- include definitions of key terms
- include questions with a range of cognitive verbs, and suitable answers (that have been checked)
- be legible!

As you work through the course material during the year, it is vital that you take detailed notes from classwork and homework. These notes will be the foundation of your revision and summary notes.

CONSOLIDATING LEARNING

Begin study early. It is easy to procrastinate and then find yourself rushing to revise and study at the last minute. Just-in-time is not a recipe for success. Learning is more effective if it is spread over a long period instead of a last-minute cram.

Learning requires discipline over the duration of the course. Repetitive and frequent revision of the course material helps to reinforce and deepen understanding and helps embed learning in your long-term memory. Studying and revising can be overwhelming. Revise manageable chunks by dividing your work into smaller sections or topics.

> Time management is important.
> Use your study time effectively.
> Use your leisure time effectively.

During the year, get into the habit of revising completed sections of the course. The revision may be done, for example, at the end of a week, a topic, a chapter or at intervals that best suit you. Revise work from earlier in the year on a regular basis. Ask your teacher for copies of any past exams you have done and use the answer/marking scheme to help you revise. It is easy to forget information if you do not keep reminding yourself.

There are a number of revision strategies you might use. Identify your own study strengths—what works best for you—then make effective use of these strengths.

Following are some effective learning routines and strategies for use throughout the year.

1. Your teacher is a chemistry expert. They are an excellent resource and should be the first person you consult for support and help. Seek help during class if you are struggling to understand concepts. If you encounter problems outside of class time, it is a good idea to write down areas that you are struggling with and consult your teacher at the next opportunity. Remember to pinpoint specific concepts or questions. Ask your teacher to re-explain concepts and ask for more material and/or questions for practice.
2. Make your own flashcards. Dedicate each card to a particular idea that could include:
   - definitions—key term on one side with the definition on the back
   - diagrams—diagram on one side with a brief explanation on the back
   - equations and formulas—formula on one side with a worked example on the back
   - graphs—graph on one side with a summary of results on the back
   - questions—question on one side with the answer on the back.

Use the cards to test yourself. Ask friends or family to test you. Periodically reading the cards reinforces learning and entrenches concepts in long-term memory (Figure 1.17.1). Flashcards are an excellent tool for the subject matter that must be remembered.

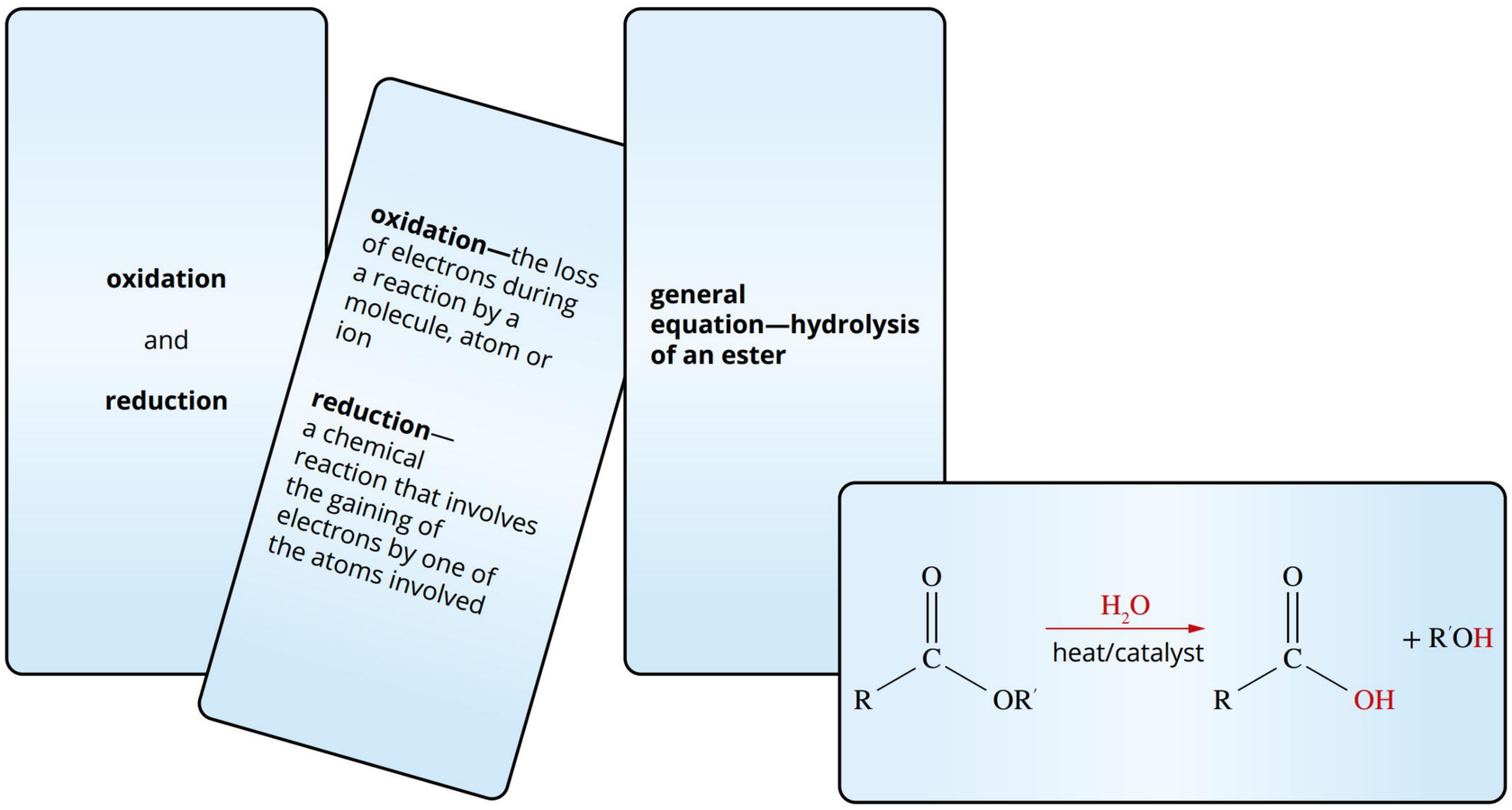

FIGURE 1.17.1 Flashcards are an excellent tool for remembering and testing yourself on factual material.

3 Trigger words. Write down the key words associated with a topic or theme. Trigger words are useful in helping to generate other related words and ideas. This approach is helpful in preparing everything from quick drafts to questions and concept maps to summarising whole topics.

4 Diagrams are useful memory triggers—draw first, label and explain second!

5 Test yourself. Complete as many questions as possible to test your learning. Handwrite (not type) your answers. Writing is a more valuable practice than just thinking about your answer. Writing is a good way to memorise material. Remember, you will need to be able to write for 90 minutes in the allocated writing time in the exam, and your writing must remain legible.

6 Summary notes. Consider your preferred learning style and take advantage of it to make revision notes. Summaries help you identify essential concepts and reinforce learning. Keep in mind that any study notes you make are most effective when they are:

- clear
- to the point
- uncluttered.

Some techniques you may apply to create useful summaries include:

- highlighting or underlining important points as you read your notes or text
- creating headings or appropriate structures under which to organise ideas, e.g. under each syllabus bullet point
- using labelled diagrams to summarise concepts
- creating tables to make comparisons (e.g. causes/effects, for/against)
- creating summary sheets
- using boxes, circles and colour to highlight points on your summary sheets
- using mnemonic devices to remember key points; for example, Oil Rig: Oxidation is loss; Reduction is gain (of electrons)
- compiling a glossary of new terms. Write the student book version and then in your own words. This helps you remember new terms.
- employing scatterplots, mind maps or concept maps to organise key information (Figure 1.17.2).

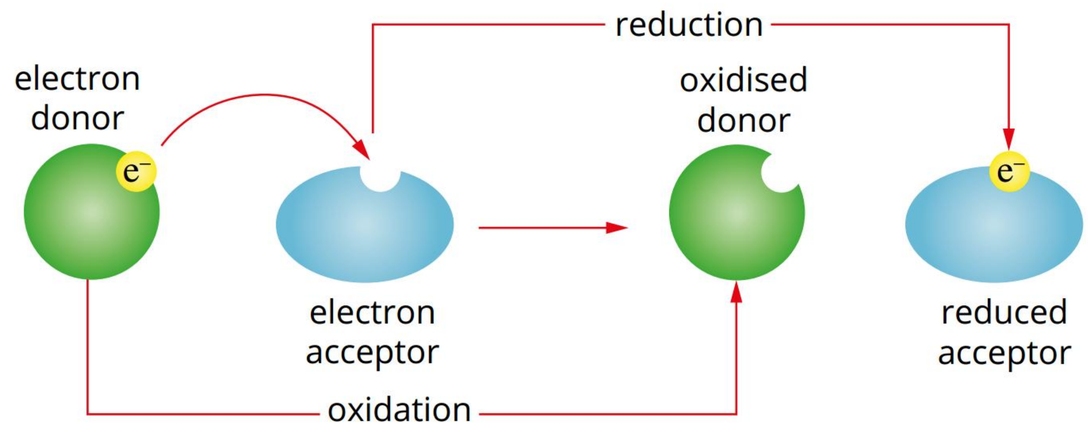

FIGURE 1.17.2 Creating visual representations in the form of concept maps is an effective revision and study tool.

7 Use chapter and module openers and module review summaries as a checklist for the key ideas in a chapter.
   - Tick those with which you feel confident.
   - Highlight those you need to revisit.
   - Reread relevant sections of text.
   - Rewrite notes, definitions or equations that you need to consolidate.

8 Form a study group with friends. The group can meet face-to-face or online. Discuss and explain key points to each other. If you are struggling with a difficult concept, try to teach it to a friend. You cannot explain something to another person until you have it clear in your own mind. Teaching and explaining to someone else makes it clearer to you.

9 Complete lots of practice questions. Write down your answers so that you get practice expressing yourself. Verbalising or thinking the answer is not the same, and your responses may not always come out in writing as you intend, unless you have plenty of practice. Check your answers with the study group, against a reliable source and with your teacher. Make sure the answers are correct and try to improve your answers to a higher level. Try allocating marks to your own answers.

10 Familiarise yourself with the data booklet. In the exam, you have access to the data booklet. Make sure that you use the data booklet throughout the year, as needed, to become familiar with when and how to use it. Print yourself a copy and keep it on hand. You will use it more in some topics than others.

11 Download the glossary of cognitive verbs (general syllabuses) provided by QCAA and refer to it when responding to practice examination questions.

12 Download and complete senior chemistry past papers from the QCAA website. Make sure to also download the relevant marking schemes. Keep in mind that these resources relate to the 2019 syllabus, and certain questions will no longer be relevant. In addition, some new 2025 syllabus topics will not be represented in these exams. Your teacher will be able to explain the difference between the science understanding content of the 2019 and 2025 syllabuses.

REVISING AND PRACTISING

In the months and weeks leading up to the exam, most, if not all, of the course will have been taught. Your focus should now shift to studying in preparation for the exam. You will be at an advantage if you have taken comprehensive notes throughout the year, made revision summaries, completed practice questions and generally made every effort to advance your understanding and skills.

Prepare a study timetable

Allocate time to study all the subject matter and start early. Study is work that you set yourself (e.g. summary notes, practice questions), which is independent of homework or assessment provided by your teacher. A study timetable may include daily or weekly study time for all your subjects and may specify sections of each subject to be covered. While you may not stick strictly to the timetable, it is a guide to fitting everything in and allocating equal time to different subjects. An early start might mean that you study Unit 3 at home while completing Unit 4 in class. Or perhaps, revise Unit 4, Topic 1 at home while completing Unit 4, Topic 2 in class.

This kind of planned study is similar to the way an athlete builds their ability over a time period – it is not possible to achieve the maximum level by training for just a few weeks before the event! In addition, you will feel more comfortable in those final few weeks with large sections of study completed.

Prepare summary notes

You should have been making summary notes of the subject matter throughout the year. It is now time to consolidate your learning across Units 3 and 4. Remember that different topics link with each other, and it is only when a whole topic or unit is completed that these links may become apparent. The notes you have prepared can be collated and will serve as a summary of Units 3 and 4. These notes are best handwritten, as you will need to practise expressing your ideas legibly for the examination.

List all the topics and subtopics in the syllabus, including the subject matter statements. The opening pages of each chapter in your student book will guide you. You might choose to prepare a separate table for each topic and use it to write your revision notes. The sample shown in Figure 1.17.3 allows for key points, formulas and key terms and definitions for each topic. While this layout may suit some students, it may not suit you. Adjust the labels and organisation to best suit you. For example, you may choose to include a column for worked examples and/or sample questions.

Unit 3 Equilibrium, acids and redox reactions			
Topic 2 Oxidation and reduction			
	Key points	**Formulas**	**Key terms and definitions**
redox reactions			
electrochemical cells			
galvanic cells			
standard electrode potential			
electrolytic cells			

FIGURE 1.17.3 A summary of revision notes in table form

Read through your student book and class notes. Identify key sections and terms. These can be added to your revision table for later elaboration. Reread your class notes carefully for a section of work. Once you feel you understand and remember them, put the notes aside. Without referring back to the notes, start filling in the revision table. You may need to keep referring back to your notes, but avoid copying them directly. Each rereading of the notes will reinforce your learning.

Refer to additional resources if you do not understand something. This might mean checking the student book, asking your teacher, researching online or discussing with classmates. You can keep track of problem areas by writing questions in the margin of the revision table, highlighting parts of the revision notes you do not fully understand, or keeping a separate queries sheet.

Use abbreviations and symbols, but remember that only standard symbols and abbreviations may be used in the chemistry exam. In order to save time and space on the revision table, you can develop your own abbreviations. Dot-point notes, visuals, tables and graphs are all useful ways of summarising information. Use these in your revision table as appropriate. It is often easier to recall information in these forms than to visualise a large block of text. If you are a visual learner, it may be helpful to colour-code your notes to emphasise different concepts. Rewriting notes, whether in note or visual form, helps you remember them.

In preparing the revision table, you read and reread the subject matter, so your understanding continually improves, and the subject matter is learned. Practise rewriting the revision table without referring to the original one. Try making a summary of the revision table so that you focus on the essential concepts. Discuss concepts with classmates to clarify your understanding. Give the revision table to a family member and ask them to test you. These are some of the strategies that can be used to reinforce your learning. Another strategy is to 'traffic light' your work. Create a list of the subject matter for Units 3 and 4, and highlight in green the concepts you are very familiar with and for which you can answer medium-to-difficult questions. Highlight in orange the concepts that you understand but can only answer easy- and some medium-level questions. Highlight in red the concepts for which you can only answer basic questions and need help from your teacher or peers.

Practise, practise, practise!

Remember the saying 'practice makes perfect' and complete as many test and exam papers as possible. Sitting an exam requires skill, and the more practise you have in advance, the more prepared you will be. Take practice exams within the time limit allocated. Handwrite your answers to get practise at working quickly, writing your ideas legibly and expressing yourself clearly. Exam paper practice will show you what you know, but more importantly, what you do not know and need to revise. Use the marking scheme after you have completed the paper, and do not be tempted to check it for a tip or hint. If you do this, you are not training your brain to work through a thought process to find the answer.

Your teacher will likely provide a mock exam for the class – reviewing your achievement here is critical to direct your final study stages and identify areas to work on. By reviewing where each mark is awarded in the marking scheme, you will become familiar with expected responses for some of the more common questions.

Remember, the QCAA past papers (two mock exams and 2020–2025 external assessments), while useful, relate to the previous syllabus, which has Units 3 and 4 concepts not in the 2025 syllabus (e.g. enzyme structure, X-ray crystallography, transesterification, and other topics). They also do not assess the new topics added in 2025 (e.g. K_{sp}, conductometric titration, Faraday's law and other topics). Your teacher will provide direction as to which questions are no longer relevant in QCAA past papers and which are 'new' topics.

SITTING THE EXAM

There will always be one more practice question or one more flashcard to write, but nominate your stopping point and give yourself credit for the work completed. Do not cram the night before the exam, but rather reread your revision table to refresh the subject matter. Check your calculator battery, pens, pencils, eraser and ruler. Use the information provided by your teacher or on the QCAA website to make sure that you only take approved equipment (Table 1.17.1). Your calculator can be a scientific or graphics calculator (with memory cleared) and must be listed on the approved calculator list on the QCAA website. Double-check the date, time and place of the exam. Try to get a good night's sleep followed by a good breakfast on exam day.

Arrive at the exam with plenty of time to spare. Running late will only create stress before you even get into the exam room. Adopt a positive attitude that you now have a unique opportunity to show your understanding of senior chemistry. Remain calm and focused as you enter the exam room.

TABLE 1.17.1 Approved equipment for senior chemistry examination (QCAA). A clear plastic container or plastic bag may be used to carry the equipment. Correction fluid/tape and erasable pens are not permitted.

black or blue pens (non-erasable)
2B pencils, a sharpener and an eraser (good quality) Note: 2B pencils are only required for multiple-choice questions and drawing graphs or diagrams. Black or blue non-erasable pens must be used for all other written responses.
Approved calculator—only calculators approved by QCAA for use in assessments are permitted. Calculators must be handheld and solar- or battery-powered. Scientific calculators must meet the requirements set out in the scientific or graphics calculator list and be cleared of memory before entering the assessment room.
highlighters—students should not highlight their responses, but may highlight stimulus or questions when permitted by the supervisor
a clear plastic ruler marked in mm
water in a clear, unlabelled bottle
asthma inhaler (if required)

There are some strategies to keep in mind during the exam that will improve your chances of doing well. Remember, you can only be asked about information that is included in the course. The exam is your opportunity to showcase your knowledge of this subject.

Perusal or reading time

Every exam allocates time for you to look over the exam paper—10 minutes for senior chemistry. You are not permitted to pick up pens, pencils or highlighters at all during this time, not even to write your identification on the answer booklet. Use this time wisely, as it is valuable for you to get an overview of the paper.

- Check through the entire paper quickly. Alert the supervisor if pages are missing/incomplete as per exam instructions.
- Carefully read the instructions and reread them.
- Plan how much time you will allocate to different sections of the paper.
- Decide in what order you will complete the questions, i.e. perhaps do the easy questions first so you have more time to complete the harder ones.
- Start reading questions and answering them mentally.
- If a question is difficult, do not dwell on it. Move on to the next question. Sometimes another question can give clues to ones that appear difficult.
- Carefully read and reread each question. In your head, translate into your own words what you are required to do. Look carefully at questions containing unfamiliar material to determine the link to the syllabus. Unfamiliar material will have sufficient explanation attached to it to allow you to use the skills you have learnt using familiar topics.
- Check for measurement units that will need converting.
- Consider the marks allocated to each question. Plan to spend more time on questions that award more marks.
- Identify the extra space and second copies of diagrams at the end of the paper – you will use these if you need to redo a question.
- Supervisors cannot respond if you think a question is written incorrectly or contains an error. Complete the paper as best you can and identify your concern at the end of working time.

Writing time

Start writing as soon as you are permitted. Keep in mind the following strategies.

Read and reread questions carefully

If you find it helpful, underline/circle key words in the question. This can be a useful strategy in identifying the focus of the question and giving direction about what is required in your answer (e.g. cognitive verb(s)). For questions with an introductory stem and parts, read the whole question before starting to write your answer. Otherwise, you may write answers for the first part that belong to later parts. Sometimes the information in one part of a question will provide a hint for another part.

Interpret questions carefully

Look for key verbs such as 'explain', 'compare' and 'determine' that tell you what you are expected to do. The questions in your student book and activity book have been written using key verbs from the syllabus, so you should be familiar with the style of questioning and will have had practice at interpreting questions. Make sure your answers address all parts of the question. Use scientific terms and give your answers to the correct number of significant figures and with a unit.

Show your working

Show all the steps you took to reach your solution on questions involving calculations (i.e. your working). While there may be an error in one part of the calculation, you may still score some marks for the correct method. Remember to always include the correct units in answers and to correctly label all graphs (x and y axes, title, units). If you do work that you think is incorrect, simply draw a single diagonal line through the response and write your answer again. If you are using the additional pages provided at the back of the exam paper, do not forget to direct the assessor to the additional page number and indicate on your response which question it refers to.

Know how to work with data

When a question includes data presented in a graph, read the labels and units on the axes, and understand the relationship shown by the graph. The title of the graph will assist with this. Use a ruler for reading graphical data accurately.

When looking at tables, read the headings of rows and columns carefully so you can understand the content of the table. They usually contain symbols and units of data. Refer to the data booklet where appropriate. You should include the proper units for each number where appropriate. If you keep track of units as you perform your calculations, it can help ensure that you express answers in terms of the proper units. Depending on the exam question, it is often possible to lose points if the units are wrong or are missing from the answer. The format of many calculating questions will provide a blank answer box (often with units), so do not forget to rewrite your final answer here.

Answer all questions

An unanswered question cannot possibly earn you any marks. It is better to make an intelligent guess that might earn some marks than not answer at all. Remember that a diagram may gain marks. When you have completed an answer, reread the question. Check that you have addressed the actual question and all parts of it. An answer that includes correct information but does not answer the question will not earn any marks. Many short-response questions are divided into parts a, b, c and d, where each part may have a different cognitive verb and require a different type of response. Credit for each part is awarded independently, so you should attempt to solve each part. For example, you may receive no credit for your answer to part a, but still receive full credit for parts b, c or d. If the answer to a later part of a question depends on the answer to an earlier part, you may still be able to receive full credit for the later part, even if your earlier answer is wrong (known as 'carried error').

Answer questions simply and concisely

Sometimes the answer to a question is simply a one-word answer (e.g. 'state' or 'identify') or a numerical reading from a graph. Providing extra information in your answer is unnecessary and can lead to irrelevant or even contradictory information. It is also an inefficient use of exam time. Where possible, use standard phrases and scientific language that neatly encapsulate meanings rather than wordy explanations. Use scientific terms and give your answers to the correct number of significant figures and with a unit. Provide only one answer to each question—never try for an each-way bet!

Use the number of lines provided in the answer booklet as a guide to how much to write. Also, use the number of marks allocated to a question or part of a question as a guide to how detailed your answer should be. Consider whether you can add more details, a diagram, clearer explanations, or make corrections to answers. An 'identify' question may be just one mark, so you need to provide only one word or a number with a unit. But 'compare' may be three marks because there are three aspects to the response (similarity, difference, significance; see Table 1.17.2). By noting the cognitive verbs during practice questions, you will become familiar with matching the expected responses and number of marks.

Pay attention to your spelling and write legibly. When trying to answer quickly, writing often becomes messy, but an assessor should not have to guess what word you have written. For example, clearly write 'propanal' so that the reader does not identify it as 'propanol'. Do not copy the question into your response as this wastes time and answer space, and does not provide an answer. Do use any scientific terms provided in the question to support your answer.

> Providing extra information in your answer is unnecessary and can lead to irrelevant or even contradictory information. It is also an inefficient use of time.

Interpret and answer the question being asked using the cognitive verb

Provide accurate information that addresses the question to attract a mark. A key aspect of this is to identify and understand the cognitive verb used in the question. Cognitive verbs indicate the type of thinking and response required and are described in the QCAA 'Glossary of cognitive verbs – general syllabuses' document. Verbs like 'explain', 'compare' and 'analyse' tell you what you are expected to do (refer to Table 1.17.2).

The questions in your student book have been written using cognitive verbs from the syllabus, so you should be familiar with the style of questioning and will have had practice at interpreting questions that use these cognitive verbs. Make sure your answers address all parts of the question.

TABLE 1.17.2 Some examples of types of responses linked to verbs. Refer to the QCAA 'Glossary of cognitive verbs'.

Cognitive verb	Thinking/response
determine	break down a concept into its components and decide or come to a resolution
evaluate	assess the strengths or value of something based on chemistry criteria
explain	describe aspects or parts of something in more detail
contrast	give an account of the differences between two or more things
compare	display recognition of similarities and differences, and recognise the significance of these similarities and differences
identify	recognise, state or name a fact, feature or item
calculate	determine or find (e.g. a number, an answer) by using mathematical processes, showing the relevant stages in the working
describe	give an account of a situation, event, pattern or process, or of the characteristics or features of something
deduce	arrive at, reach or draw a logical conclusion from reasoning and the information given
distinguish	recognise as distinct or different; note points of difference between; make clear the difference/s between two or more concepts or items
predict	give an expected result; suggest what may happen based on available information

The following examples show that a statement can be correct but gain no marks because the desired response is not provided.

Example: ***Explain requires more detail to make clear the 'how' and 'why'***

Question: Using Le Châtelier's principle, explain why decreasing the temperature of an equilibrium with an exothermic forward reaction increases the amount of product formed.

Answer 1: Le Châtelier's principle is used to predict changes to the position of an equilibrium. ***No marks***

Answer 2: Le Châtelier's principle states that an equilibrium shifts to oppose the change. So, if the temperature is decreased, the equilibrium will shift to favour the direction that generates heat (increases the temperature). That is, the exothermic reaction. So, if the exothermic reaction is in the forward direction, then this will increase the concentration of products formed. ***Receives marks***

Although correct, answer 1 is not enough as the question asks for an explanation—because 'explain' asks for chemical detail. In this case, the detail required is the relationship between the temperature decrease of an exothermic reaction and the amount of product formed. An explanation requires a statement of the chemistry concept but must also include the 'how and why'.

Example: ***Evaluate requires details about the importance of a contributing factor to an outcome***

Question: Evaluate the following statement: Alcohols have higher boiling points than an alkane of similar molar mass.

Answer 1: It is correct. ***No marks***

Answer 2: It is correct. The boiling point of a compound is related to the strength of the intermolecular bonds between neighbouring molecules. Because the electronegativity of the oxygen atom is much less than the electronegativity of a hydrogen atom, alcohols contain a very polar OH group. This functional group is capable of forming hydrogen bonds with an OH group in a neighbouring alcohol molecule. Because the electronegativities of C and H are very similar, there is almost no charge separation in the C–H bond. Therefore, alkanes can only have temporary dipoles and so only form weak Van der Waals forces. Since hydrogen bonds are much stronger than Van der Waals bonds, more energy is required to separate the molecules. Therefore, alcohols have higher boiling points than alkanes of a similar molar mass. ***Receives marks***

Although correct, answer 1 does not contain enough information—'evaluate' asks for chemical criteria that have led to the decision.

Answer with clarity

There should be no room for interpretation, so be clear about what you mean to say.

Example: ***Identify requires a specific response***

Question: State the trend evident in the solubility curve of potassium nitrate.

Answer 1: temperature affects the solubility of potassium nitrate ***Not clear***; no marks

Answer 2: an increase in temperature causes an increase in solubility of potassium nitrate ***Clear and correct for 1 mark***

Know how to tackle multiple-choice questions

Multiple-choice questions are designed to make you select between very similar or opposite items. Read all options carefully. If you are unsure, start by eliminating answers you know to be incorrect. Make your final choice from the possible answers that remain. Answer every multiple-choice question, even if all you can do is guess. You should answer each multiple-choice question before you move on to the next one. You can mark a question to come back to later if you have time, but you should still fill in an answer before you move on. You should allow just over a minute for each question. If the question takes longer than that, take a guess and move on.

Multiple-choice answers are completed by filling in the bubbles on a separate answer sheet (the first page of Paper 1). Answers written or circled on the question booklet are not marked. Make sure that you mark your answers on the answer sheet using a 2B pencil (which is easy to erase if needed).

Come back to difficult questions

If you find a question particularly difficult, skip it. Come back to it later if you have time. You should never use the 'scattershot', 'brain dump' or 'laundry list' approach, i.e. writing answers with as many terms and facts as you can, hoping that the correct one will be among them. Your answers need to be well organised and relevant—take a few moments to plan before writing longer responses.

Have a plan to deal with mental blocks

Sometimes, in conditions when you are under pressure, your mind can go blank. The information is there, but temporarily not available to you. Take a few deep, slow breaths. Try to visualise your notes on the revision table you created. If this does not work, move on to another question and return to this question later. Often, answering a further question will jog your memory on the topic, and you will be able to provide the answer on the second try. It is useful to have a system for annotating which questions need to be revisited—you may quickly write the issue which has caused the 'block' as a reminder.

Recheck your answers

If you have time, return to questions that you are unsure of. There is no need to check all answers if you run out of time. Reread each question when you have finished answering it. Focus on the information or answer requested and the cognitive verb in the question. These two aspects will help you to be sure that you have addressed every part of the question to the correct cognitive level.

Double-check reasoning in non-numerical answers—you may have made an error that could change the meaning of your response. This is especially true when your reasoning uses several stages. An example of this would be explaining that the concept of evolution by natural selection starts from having genetic variation in a population (not from the acquisition of characteristics).

Never leave the exam early

Exams are generally designed to take the full writing time allocated to them. If you finish early, recheck for anything you may have missed. Check for blank pages and both sides of the page to make sure you have not missed anything! Count the number of questions you have answered against the number listed on the front of the exam paper.

Do not leave a question blank—have a guess! No marks will be deducted for an incorrect answer, but you may pick up marks for a partial response. Also, if you are unsure of a multiple-choice answer, try to eliminate one or more of the options, then have a guess. You may be lucky!

AFTER THE EXAM

Once you have left the exam room, avoid talking to other students about the exam. Everyone has an opinion on their own personal performance. Listening to others can be unsettling. Whether you feel you performed well or are disappointed with your performance, it is now beyond your control. Consider writing a 'debrief' that describes the question(s) you answered best and one that you are unsure of. Remain calm and look forward to downloading the papers and marking scheme when they are available during Term 1 of the next year. It is one exam result, in one subject, in one year of your life. No matter what happens, there are plenty of career pathways to pursue.

Remember:

- You can only be asked about information that is included in this course. A new context may be used, but it will have a link to Unit 3 or 4.
- The exam is your opportunity to showcase your knowledge of this subject.

UNIT 3 Equilibrium, acids and redox reactions

TOPIC 1 Chemical equilibrium systems

TOPIC 2 Oxidation and reduction

Unit 3 objectives

- Describe ideas and findings about chemical equilibrium systems and oxidation and reduction.
- Apply understanding of chemical equilibrium systems and oxidation and reduction.
- Analyse data about chemical equilibrium systems and oxidation and reduction.
- Interpret evidence about chemical equilibrium systems and oxidation and reduction.
- Evaluate processes, claims and conclusions about chemical equilibrium systems and oxidation and reduction.
- Investigate phenomena associated with chemical equilibrium systems and oxidation and reduction.

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CHAPTER

02 Chemical equilibrium

In this chapter, you will investigate the ideas of reversibility and irreversibility of chemical systems. This study of reversible reactions will introduce the concept of chemical equilibrium.

Various factors can change the position of a chemical equilibrium. Le Châtelier's principle enables scientists to understand the effects of changes in concentrations in solutions, pressures of gases and temperature on an equilibrium.

The fact that many reactions do not proceed to completion is of vital importance in nature, including the metabolic processes that occur within the human body and other reactions in the biosphere. It also has serious consequences on the efficiency of many chemical manufacturing industries. You will learn how reaction conditions affect the relative quantities of reactants and products in an equilibrium system.

You will also learn how to write a mathematical relationship, known as an equilibrium law expression, for an equilibrium reaction. This law can be used to calculate the concentrations of reactants and products when a reaction is at equilibrium.

Syllabus subject matter

Topic 1 • Chemical equilibrium systems

CHEMICAL EQUILIBRIUM

- Discriminate between open or closed chemical systems. **2.1**
- Identify that physical changes are usually reversible, whereas only some chemical reactions are reversible. **2.1**
- Symbolise equilibrium equations using $\rightleftharpoons$ in balanced chemical equations. **2.1**
- Explain observable properties and the characteristics of physical and chemical systems in a state of equilibrium. **2.1**
- Explain that, over time, physical change and reversible chemical reactions reach a state of dynamic equilibrium in a closed system, with the relative concentrations of products and reactants defining the position of equilibrium. **2.1**
- Explain the reversibility of chemical reactions by considering the activation energies of the forward and reverse reactions. **2.1**
- Analyse data and interpret graphical representations of relative changes in the concentration of reactants and products against time to determine the position of equilibrium. **2.1**

FACTORS THAT AFFECT EQUILIBRIUM

- Determine the effect of temperature change on chemical systems at equilibrium by considering the enthalpy change for the forward and reverse reactions. **2.3**
- Explain the effect of changes in temperature, concentration and pressure on chemical systems at equilibrium by applying collision theory to the forward and reverse reactions. **2.2, 2.3**

- Apply Le Châtelier's principle to determine the effect changes in temperature, concentration of chemicals, pressure and the addition of a catalyst have on the position of equilibrium and on the value of the equilibrium constant. **2.4**

EQUILIBRIUM CONSTANTS

- Identify that the equilibrium constant (K_c) indicates the relationship between product and reactant concentrations at equilibrium. **2.4**
- Identify that the solubility product (K_{sp}) gives a measure of the solubility of an ionic compound. **2.4**
- Determine the equilibrium law expression for homogeneous and heterogeneous systems. **2.4**
- Determine the extent of a reaction from the magnitude of the equilibrium constant (K_c). **2.4**
- Calculate the reaction quotient (Q) for reversible reactions (Formula: $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ for the reaction $aA + bB \rightleftharpoons cC + dD$). **2.4**
- Calculate equilibrium constants (K_c) and the concentrations of reactants and products. Assume that $[\text{reactants}]_{\text{initial}} = [\text{reactants}]_{\text{equilibrium}}$ when K_c is very small, and state the assumption when used. (Formula: $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ for the reaction $aA + bB \rightleftharpoons cC + dD$). **2.4**
- Calculate solubility products (K_{sp}) and the concentrations of ions in aqueous solutions. (Formula: $K_{sp} = [C]^c [D]^d$ for the reaction $aA(s) \rightleftharpoons cC(aq) + dD(aq)$). **2.4**
- Infer shifts in equilibrium reactions using equilibrium constants (K_c) and reaction quotients (Q). **2.4**
- Analyse data to determine reaction quotients (Q), equilibrium constants (K_c), concentrations of reactants and products and the concentration of ions in aqueous solutions. **2.4**

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Revision

In Units 1 and 2, you covered the content that forms the background required to successfully complete this chapter. To assist you in understanding the content of this chapter, the following key concepts are revisited in summary:

- energy changes in chemical reactions
- rates of reaction.

Reviewing this content should not be factored in as part of the notional hours for Chapter 2.

ENERGY CHANGES IN CHEMICAL REACTIONS

All substances have **chemical energy**. The chemical energy of a substance is the sum of its potential energy and kinetic energy. These energies result from such things as attractions between electrons and protons in atoms, repulsions between nuclei, repulsions between electrons, movement of electrons, and vibrations of and rotations around bonds. The chemical energy of a substance is also called its **enthalpy**, and is given the symbol H.

During a chemical reaction, the atoms in the reactants are rearranged into products with different chemical energies. The reaction can be **exothermic** or **endothermic** depending upon the relative energies of the reactants and products. The energy released or absorbed during a chemical reaction is called the **heat of reaction** (symbol ΔH). For exothermic reactions, $\Delta H < 0$, and for endothermic reactions, $\Delta H > 0$.

The energy required to break the bonds of reactants so that a reaction can proceed is called the **activation energy**.

Thermochemical equations

Thermochemical equations show the energy released or absorbed during a chemical reaction, symbol ΔH. Energy is usually measured in joules (J) or kilojoules (kJ) and the ΔH value has the units $\mathrm{J\,mol^{-1}}$ or $\mathrm{kJ\,mol^{-1}}$. This means that the energy shown by the ΔH value corresponds to the mole quantities specified by the coefficients in the equation. Remember:

- when the coefficients of an equation change, the ΔH value changes by the same factor
- when the equation is reversed, the sign of the ΔH value is reversed
- states of matter must be shown in thermochemical equations because changes of state involve enthalpy changes.

RATES OF REACTION

The rate of a chemical reaction can be determined by measuring the change in concentration of the reactants or products with time. As the reaction conditions change, the rate of reaction will change.

There are five main ways in which reaction rate can be increased: increasing the concentration of solutions, increasing the pressure of gases, increasing the surface area of a solid reactant, increasing the temperature and using a **catalyst**.

Collision theory

For a chemical reaction to occur, the particles involved must collide with each other with sufficient energy to overcome the activation energy 'barrier' to the reaction. This way of visualising reactions is known as **collision theory**.

Only 'successful' collisions, where the energy of collision is greater than the activation energy, allow a chemical reaction to progress. So, the rate of a chemical reaction is also dependent on the proportion of collisions that are successful.

According to collision theory, for a reaction to occur, the reactant particles must collide with each other, and have an energy that is equal to, or greater than, the activation energy so that collisions break or weaken the bonds within the reactants and allow products to form.

2.1 Dynamic equilibrium

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- distinguish between open and closed systems
- appreciate why some reactions are described as reversible
- understand how reversible reactions in a closed system reach a dynamic equilibrium
- recognise that the extent of reaction can be different for different equilibria.

In this module, you will learn that some chemical reactions can occur in both the forward and reverse directions. These reactions are called 'reversible reactions'.

Reversible chemical systems are encountered in many everyday situations, including chemical manufacturing processes, the reactions of ions within individual cells in your body and the reactions carbon dioxide undergoes in the environment.

This module also describes how some reversible reactions can reach a point where they appear to 'stop'. At this point, the concentrations of the reactants and products remain constant, even though there are still reactants remaining.

The fact that many reactions do not proceed to completion has important consequences for the production of chemicals by industry. The presence of large amounts of unreacted starting materials in reaction mixtures is wasteful and costly. The profitability of an industry depends on the yield—the extent of conversion of reactants into products.

Although these reactions appear to stop, they actually continue to proceed. If you could see what was occurring at the atomic scale, you would notice that as rapidly as the reactants are forming products, the products are re-forming reactants. This situation can be likened to the queue shown in Figure 2.1.1. Although the length of the queue may seem constant, people at the front are continually leaving the queue and others are joining it at the back at the same rate.

FIGURE 2.1.1 A queue of constant length can be likened to a reaction that appears to have stopped. People leave the queue at one end at the same rate as others join it at the other end.

OPEN AND CLOSED SYSTEMS

In Units 1 and 2, you learnt that a chemical reaction can be regarded as a **system**, with everything else around it (the rest of the universe) being the surroundings. In an endothermic reaction, the system absorbs energy from the surroundings, whereas in an exothermic reaction, energy is released to the surroundings.

Figure 2.1.2 illustrates how you can distinguish between the two different types of systems:

- **open systems**
- **closed systems**.

In a closed system, only energy can be exchanged with the surroundings.

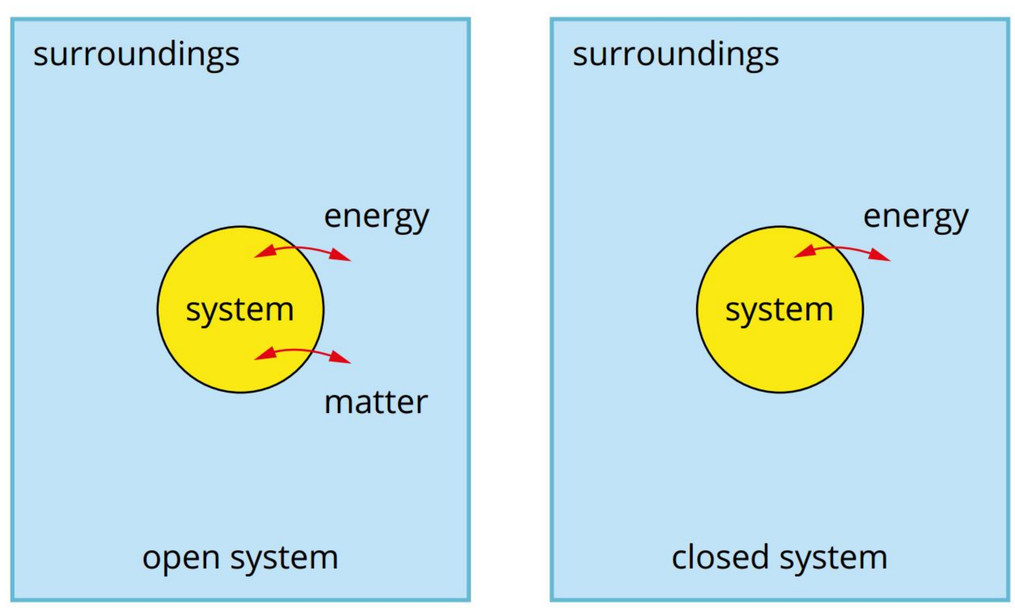


FIGURE 2.1.2 Open systems exchange energy and matter with the surroundings. Closed systems exchange only energy with the surroundings.

The most common situation in everyday life is an open system. In an open system, matter and energy can be exchanged with the surroundings. In contrast, a closed system exchanges only energy with the surroundings.

Some examples of open and closed systems are illustrated in Figure 2.1.3.

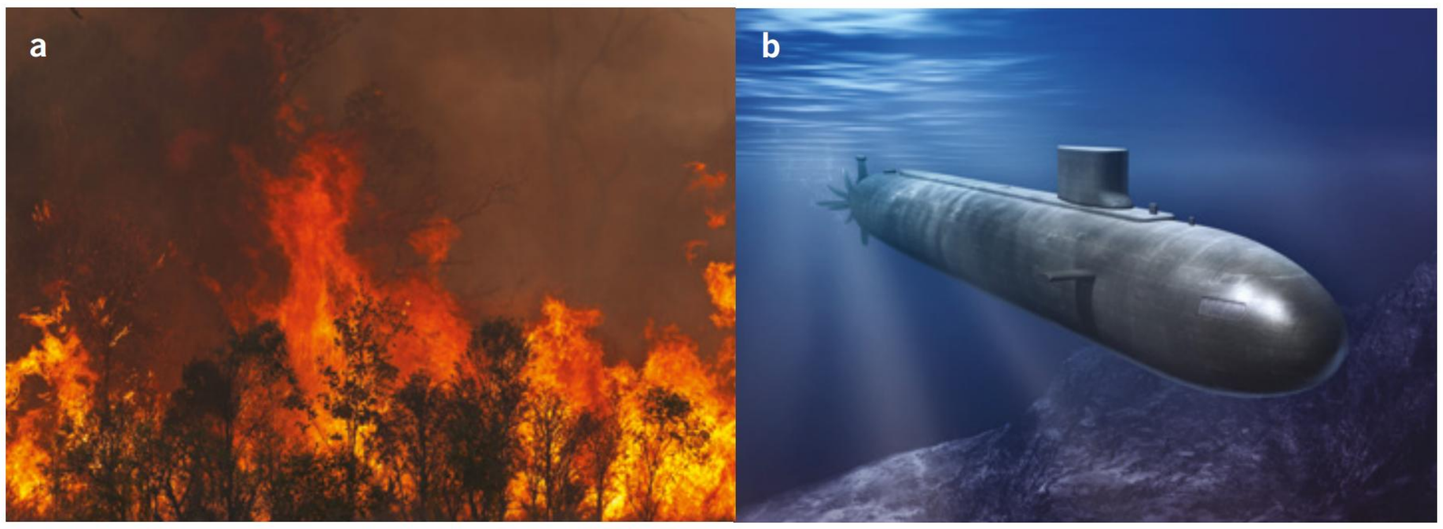


FIGURE 2.1.3 Everyday examples of open and closed systems. (a) A bushfire burning through a forest in south-west Queensland. This is an example of an open system. Carbon dioxide and water vapour produced by the burning trees are released into the atmosphere. (b) A nuclear submarine in operation under water—the carefully monitored environment of the submarine can be regarded as a closed system.

IRREVERSIBLE AND REVERSIBLE SYSTEMS

You may have thought, as a younger student, that when chemical reactions occur, the reactants form products and these products cannot be converted back to the reactants. Such reactions, which occur only in one direction, are called non-reversible or **irreversible reactions**.

Baking a cake, like the one shown in Figure 2.1.4, involves several irreversible reactions. The reactions are complex and include reactions that change the chemical structures of the protein in flour and egg, as well as reactions between protein and sugars.

FIGURE 2.1.4 Baking a cake involves a series of irreversible chemical reactions.

Combustion reactions, such as the burning of methane, are also irreversible:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Once a fuel has burnt, the products, carbon dioxide and water, do not react with each other to re-form methane and oxygen under normal conditions.

As you will see, other reactions are **reversible reactions** where the products, once formed, can react together to re-form the reactants.

Reversibility of physical and chemical changes

Four examples of systems that are reversible are:

- evaporation and condensation of water
- a saturated sugar solution
- oxygen transport in the blood
- synthesis of ammonia.

These examples are described below.

Evaporation and condensation of water

You are familiar with the idea that a physical change, such as a state change, can be reversed. The evaporation of water from lakes and rivers leading to cloud formation and eventually rain is an example of a physical change. Water can cycle between the different states of solid, liquid and gas because each change of state process is reversible.

The evaporation of water can be expressed by the equation:

$$H_2O(l) \rightarrow H_2O(g)$$

The condensation of water can be expressed by the equation:

$$H_2O(g) \rightarrow H_2O(l)$$

Equilibrium is not achieved in an open system.

Equilibrium is achieved in a closed system when the rates of the forward and reverse processes are equal.

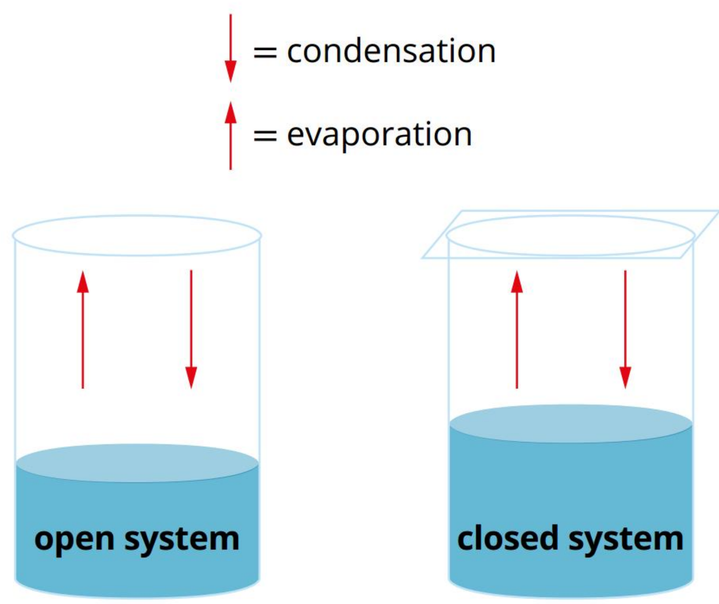


FIGURE 2.1.5 A physical change—the evaporation and condensation of water—in open and closed systems. In the open system, all the water eventually evaporates.

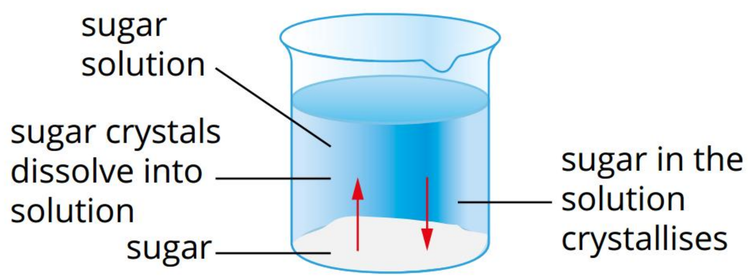


FIGURE 2.1.6 A representation of the processes occurring in a saturated sugar solution.

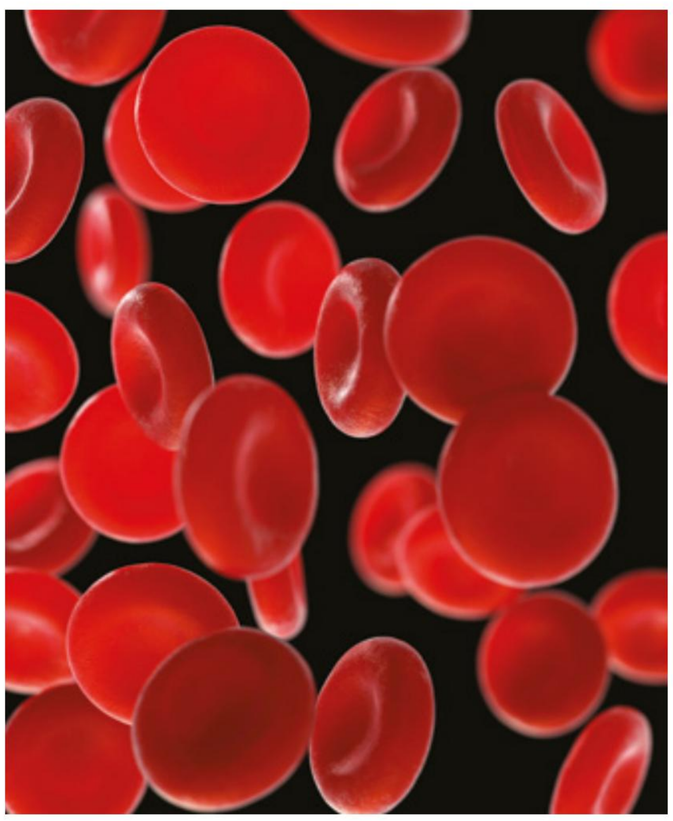


FIGURE 2.1.7 Blood cells contain a red pigment, haemoglobin, that transports oxygen from the lungs to other cells in the body.

In chemistry, a double arrow ($\rightleftharpoons$) is used when writing a chemical equation to show a reversible process. In this way, you can show the above state changes associated with water using the following equation:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

As you can see in the diagram of water in two glasses in Figure 2.1.5, these changes of state can occur in either open or closed systems. In a closed system, the water vapour cannot escape. In general, reversible processes in a closed system eventually reach a situation where the rates of the forward and reverse processes are equal. At this point, there will appear to be no further change to the observer. The system is described as having reached a state of **equilibrium**.

However, in an open system, although water can evaporate and condense, the rate of each process is not equal. Gaseous water molecules are escaping into the atmosphere, so the rate of the reverse reaction (condensation) does not become equal to the rate of the forward reaction. Equilibrium is not achieved in an open system.

Saturated sugar solutions

A **saturated solution** contains the maximum amount of solute that can be dissolved in a solvent. Consider a saturated solution of sugar in contact with undissolved sugar crystals at a constant temperature, as shown in Figure 2.1.6.

Even though it appears to an observer that nothing is happening, on a molecular level, the molecules are constantly in motion and exchanging between the solid and solution phases. The sugar molecules ($C_{12}H_{22}O_{11}$) are dissolving at the same rate as they are crystallising, and the mass of sugar crystals present is constant. The process is reversible and at equilibrium. It can be represented by the equation:

$$C_{12}H_{22}O_{11}(s) \rightleftharpoons C_{12}H_{22}O_{11}(aq)$$

Although there is no lid on the beaker, this system can still be regarded as a closed system. No gas is involved, so there is no loss of the reactant or product molecules to the surroundings.

Haemoglobin and oxygen gas

Haemoglobin is a large protein molecule that is the pigment in red blood cells, as shown in Figure 2.1.7. It is responsible for the transport of oxygen from your lungs to the cells in the body. When you inhale, oxygen from the air combines with haemoglobin in the small blood vessels in the lining of the lungs to form oxyhaemoglobin:

$$\text{haemoglobin} + \text{oxygen} \rightarrow \text{oxyhaemoglobin}$$

The reaction between haemoglobin and oxygen gas is a reversible chemical reaction. The oxyhaemoglobin is transported through the blood system to other cells in the body, where oxygen is released:

$$\text{oxyhaemoglobin} \rightarrow \text{haemoglobin} + \text{oxygen}$$

The oxygen is used by cells for respiration, to provide energy for the body.

The reaction can therefore be written as:

$$\text{haemoglobin} + \text{oxygen} \rightleftharpoons \text{oxyhaemoglobin}$$

Although this can be regarded as an open system overall, an equilibrium is established in the blood as it flows through the body. During this period, it may be thought of as a closed system because there is no loss of reactants or products to the surroundings.

Synthesis of ammonia

The production of ammonia from nitrogen gas and hydrogen gas is known as the Haber process. (This process will be covered in more detail in Module 12.1.) The main reaction in the Haber process is reversible and can be represented by the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Suppose you mix 1 mole of nitrogen gas and 3 moles of hydrogen gas in a sealed container. From the equation, you might expect that 2 moles of ammonia would eventually be formed. However, no matter how long you wait, the reaction seems to 'stop' when much less than 2 moles of ammonia is present, as shown in Figure 2.1.8.

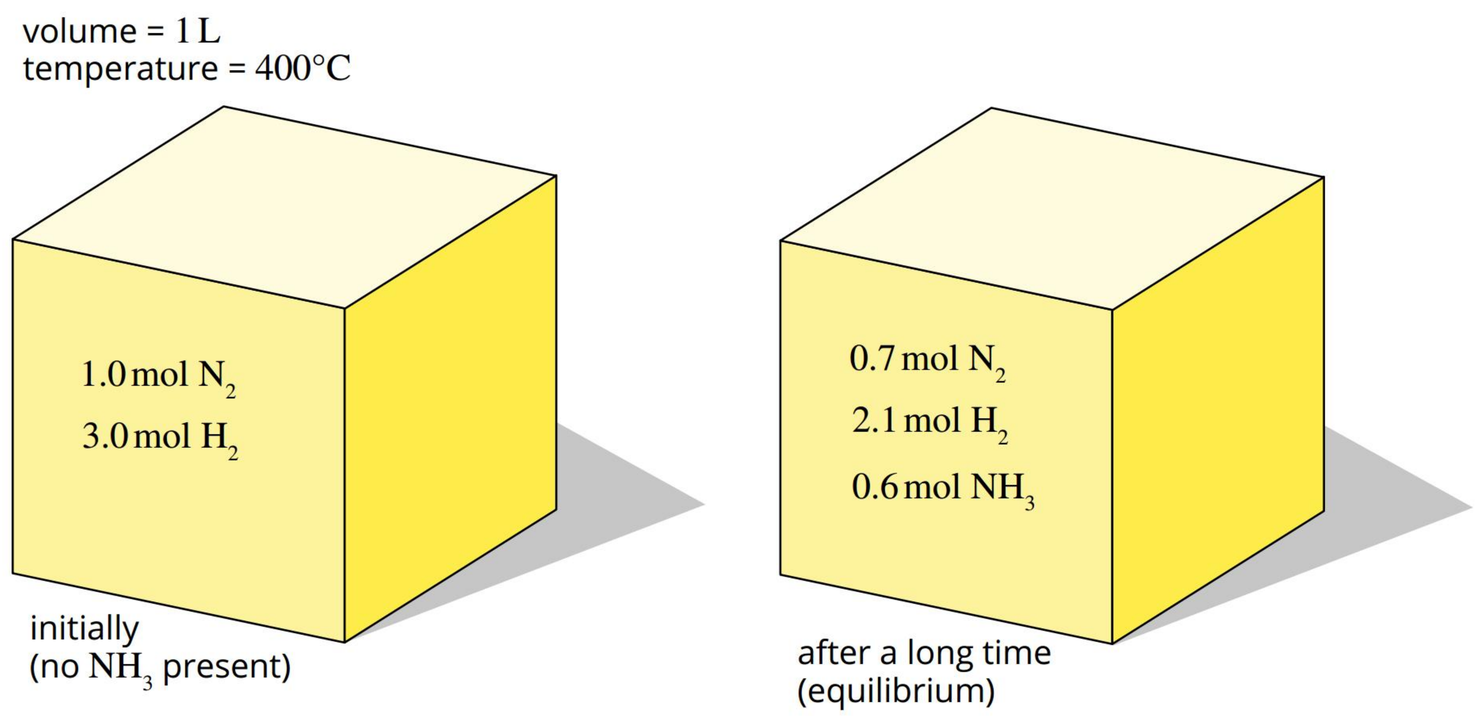


FIGURE 2.1.8 When 1 mole of nitrogen and 3 moles of hydrogen are mixed, the reaction to form ammonia appears to stop before all the reactants are consumed.

The reaction vessel in this process creates a closed system from which the reactants and products cannot escape. Once some products are formed, as a result of collisions between reactant particles, then the collisions between product particles can result in the reactants being re-formed. The reaction eventually reaches a situation where the rate of the forward reaction and the rate of the reverse reaction are equal, and an equilibrium is formed.

As for our earlier examples, when a reaction reaches equilibrium, there appears to be no further measurable change and the reaction appears to have 'stopped'. At equilibrium, significant amounts of reactants may still be present in the system.

Explaining reversibility

The reason reversible reactions can occur can be understood by referring to **energy profile diagrams**, which represent the energy changes that occur during chemical reactions.

When particles collide, the energy associated with collisions can break bonds in the reacting particles, allowing them to rearrange to form new products. The energy required to break or weaken the bonds of the reactants for the reaction to occur is known as the activation energy of the reaction.

You can see from the energy profile diagram shown in Figure 2.1.9 that once products form, if these product particles collide with enough energy to break their bonds (equal to the activation energy of the reverse reaction), then it is possible to re-form the original reactants.

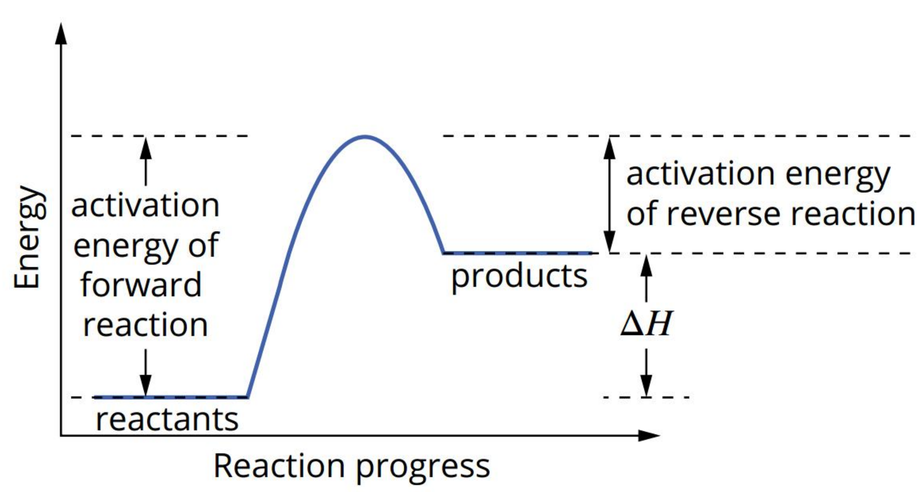
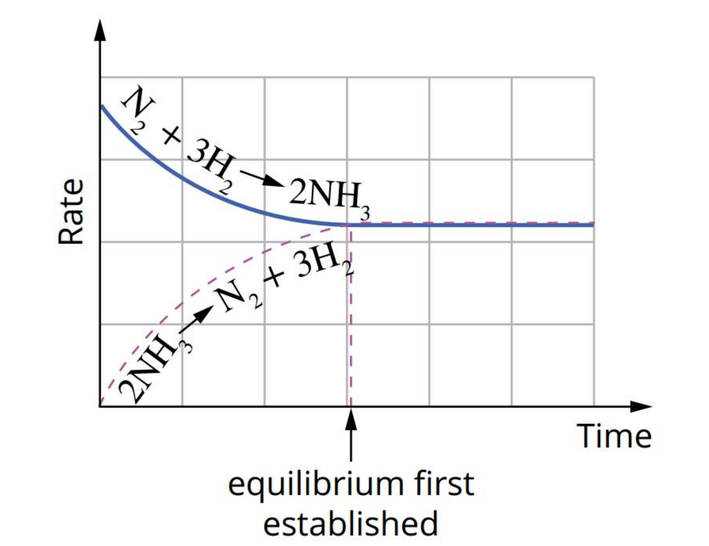


FIGURE 2.1.9 An energy profile diagram for an endothermic reaction showing the activation energy required for both the forward reaction (formation of products) and the reverse reaction (re-formation of reactants).

Note that if the forward reaction is endothermic, the reverse reaction will be exothermic, and vice versa.

EXPLAINING EQUILIBRIUM

Because the reaction between nitrogen and hydrogen to form ammonia is a reversible reaction, it is best written using equilibrium arrows:



$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Equilibrium arrows indicate that the reaction can occur in both the forward and reverse directions. These arrows should not be used where the reaction is irreversible and can only proceed in one direction.

The idea that processes can be reversed can be used to understand why this reaction reaches equilibrium. When nitrogen gas and hydrogen gas are added to a sealed container at a constant temperature, a sequence of events occurs, which can be illustrated by a plot of reaction rate versus time, as shown in Figure 2.1.10.

FIGURE 2.1.10 The variation of the rates of the forward and reverse reactions with time when nitrogen gas and hydrogen gas are mixed.

If you consider the graph in Figure 2.1.10, you can understand the following:

- Nitrogen gas and hydrogen gas molecules collide with each other and form ammonia. As the forward reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, proceeds, the concentrations of nitrogen and hydrogen decrease, so the frequency of collisions between molecules decreases and the rate of the production of ammonia decreases.
- At the same time, as ammonia is being formed, some ammonia molecules collide and decompose to re-form nitrogen and hydrogen: $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$.
- Eventually the forward and reverse reactions proceed at the same rate. When this situation is reached, ammonia is formed at exactly the same rate as it is breaking down. The concentrations of ammonia, nitrogen and hydrogen then remain constant. To an observer, the reaction now appears to have stopped with no observable or measurable change.

In a closed system at constant pressure and temperature, no further observable change will take place. The reaction has reached a point of balance—an equilibrium.

The concentration versus time graph in Figure 2.1.11 shows the changes in concentrations of the chemicals with time. Equilibrium is established when there is no longer any change in any of the concentrations.

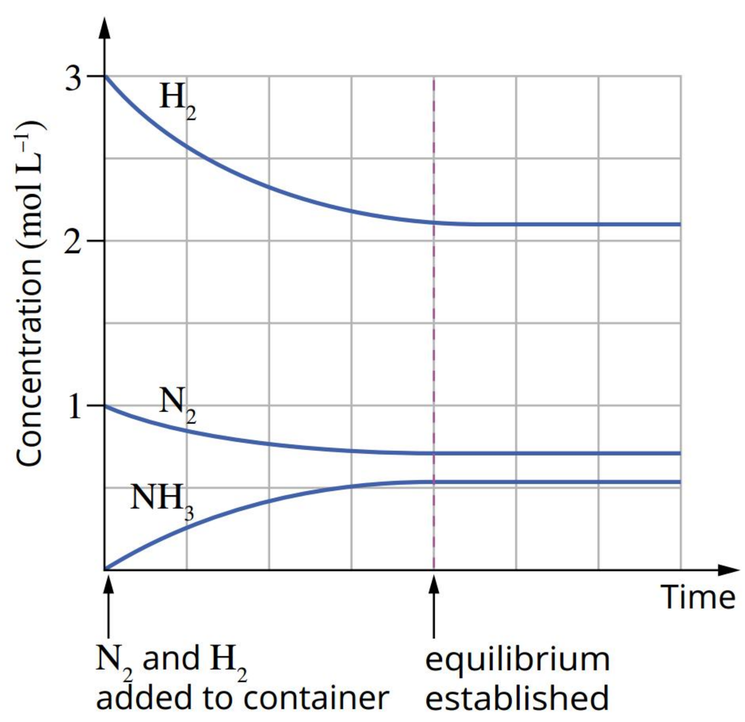


FIGURE 2.1.11 Changes in the concentrations of N_2, H_2 and NH_3 as a mixture of nitrogen gas and hydrogen gas reacts. As indicated by the coefficients of the equation for the reaction, for every mole of N_2 that reacts, three times as much H_2 reacts and twice as much NH_3 is produced.

When considering graphs involving equilibrium systems, always check if the data is presented as a plot of concentration versus time (as in Figure 2.1.11), or as a plot of reaction rate versus time (as in Figure 2.1.10).

Dynamic state of equilibrium

Chemical equilibrium can be described as being in a dynamic state because the forward and reverse reactions have not ceased. Instead, they occur simultaneously at the same rate.

During **dynamic equilibrium**:

- the reaction can be considered as 'incomplete' since *all* of the substances (reactants *and* products) are still present in the equilibrium mixture
- at the molecular level, bonds are constantly being broken and new bonds are being formed as the reactants and products continue to be converted from one to another.

The decomposition of dinitrogen tetraoxide (N_2O_4) to nitrogen dioxide (NO_2) is an example of a reversible reaction that reaches a dynamic equilibrium. The progression of this reaction from pure N_2O_4 to the equilibrium mixture containing both N_2O_4 and NO_2 can be monitored through the changing colour of the gases in the reaction vessel. N_2O_4 is colourless and NO_2 is dark brown.

The reaction occurs according to the following equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Figure 2.1.12 illustrates the observations made of a reaction vessel that is injected with some pure N_2O_4. As the forward reaction proceeds, the formation of a dark brown gas is observed. The depth of colour increases until equilibrium is reached, at which point there is no further change in the colour.

Dynamic equilibrium is reached by reversible physical or chemical processes taking place in a closed system.

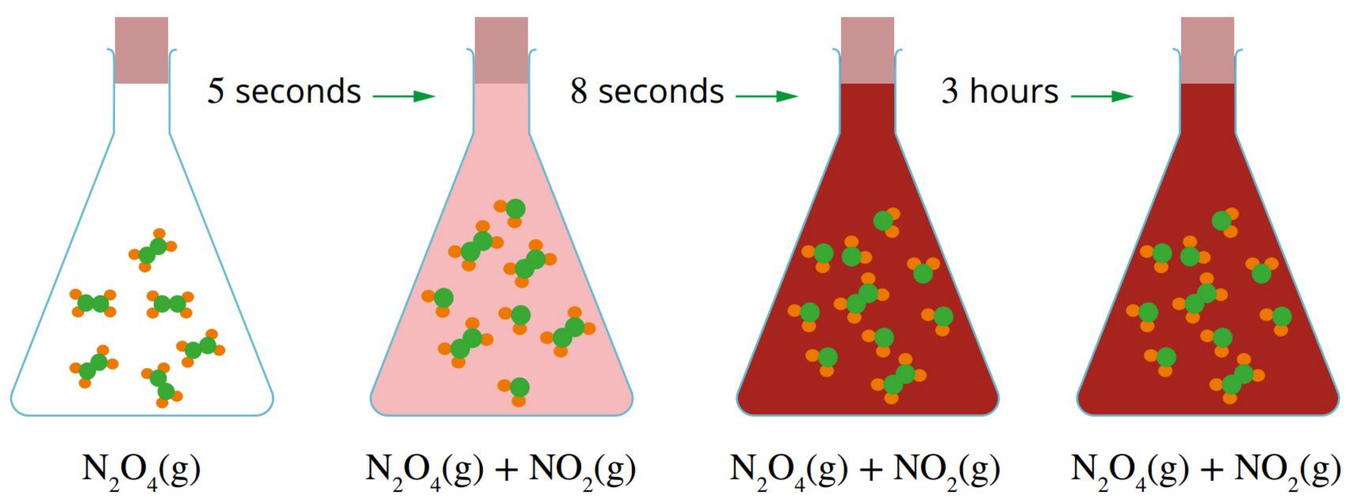


FIGURE 2.1.12 The decomposition of dinitrogen tetraoxide produces the brown gas nitrogen dioxide. As the concentration of nitrogen dioxide increases, the colour deepens until equilibrium is reached. At equilibrium (after 8 seconds), there is no further change in colour regardless of how long the reaction is allowed to proceed.

EXTENT OF REACTION

You have seen that reactions are reversible, but do all reactions proceed to the same extent before they reach equilibrium? This can be answered with a simple experiment.

You saw in Unit 2 (and will again see in Module 3.2), both hydrogen chloride (HCl) and ethanoic acid (CH_3COOH) react with water to form ions, according to the equations:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Solutions of both chemicals conduct electricity because they contain mobile ions. The relative conductivity of the solutions is proportional to the number of free ions in the solution. By measuring the electrical conductivity of solutions of the same concentration, you can compare how much each compound ionises in water.

Figure 2.1.13 shows the results obtained from such an experiment. You can see that the solution formed when hydrogen chloride dissolves in water (called hydrochloric acid) is a much better electrical conductor than the ethanoic acid solution. Both solutions were formed by adding the same number of moles of acid to identical volumes of water.

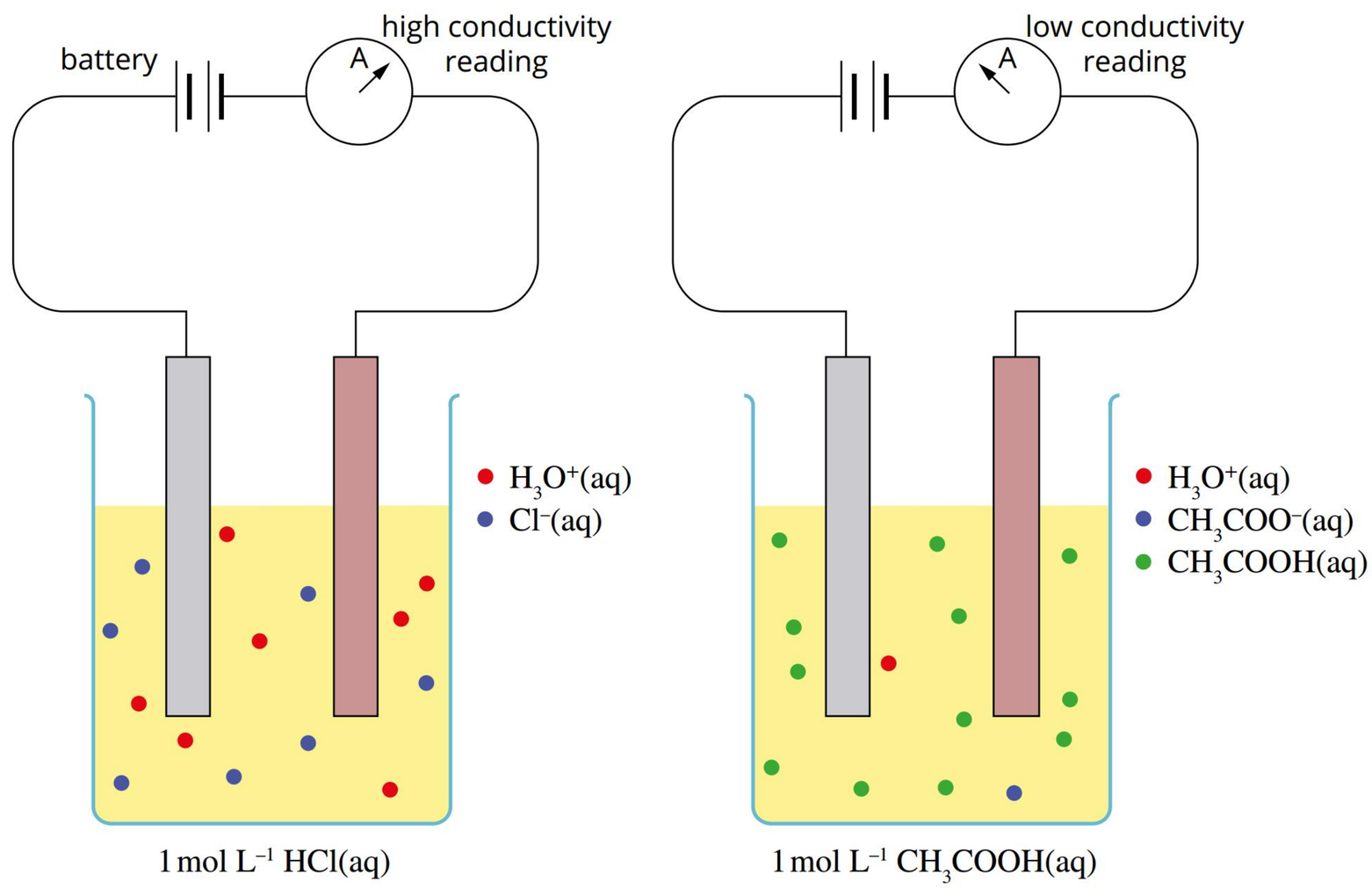


FIGURE 2.1.13 This experiment compares the electrical conductivity of 1 mol L^{-1} solutions of hydrochloric acid and ethanoic acid.

As you will remember from Unit 2, ethanoic acid is a weak acid and will therefore only partially ionise in an aqueous solution. Hydrochloric acid is a strong acid that almost completely ionises in aqueous solution. The concept of equilibrium allows us to better explain the idea of strong and weak acids by looking at the extent of the ionisation reaction (see Module 3.2).

The difference in conductivity observed in the experiment arises because these reactions occur to remarkably different extents. At equilibrium in a 1 mol L^{-1} solution, at 25°C, almost all the HCl molecules are ionised, whereas only approximately 1% of the CH_3COOH molecules are ionised.

We can conclude that different reactions proceed to different extents. The ratios of reactants to products are different for different equilibrium systems.

It is important to note that the **extent of reaction** describes how much product is formed when the system reaches equilibrium. However, the **rate of reaction** is a measure of the change in concentration of the reactants and products with time and is not directly related to the extent of reaction. The rates of reversible reactions range from very slow to very fast and determine how long the reaction takes to reach equilibrium.

The extent of a reaction does not give any information about how fast a reaction will proceed. It only indicates how much product is formed once the system is at equilibrium.

2.1 Review

SUMMARY

- In a closed system, only energy, not matter, is exchanged with the surroundings.
- In an open system, both matter and energy are exchanged between the system and the surroundings.
- A reversible reaction is a reaction in which the products can react together to be converted back to the reactants.
- An irreversible reaction is a reaction in which the products cannot react together to be converted back to the reactants.
- A double arrow ($\rightleftharpoons$) is used when writing a chemical equation to show a reversible process.
- Reversible reactions in a closed system will reach a point where the rate of the forward reaction and the rate of the reverse reaction are equal. At this point, a dynamic equilibrium has been achieved.
- Equilibrium can be achieved in closed systems but not in open systems.
- Different reactions proceed to different extents.
- The relative ratio of reactants to products when equilibrium is reached is different for different reactions.
- The extent of reaction indicates how much product is formed at equilibrium, whereas the rate of reaction is a measure of the change in the concentrations of the reactants and products with time.

KEY QUESTIONS

Describe

1 Select the correct response in the statements about chemical equilibria.

a An **open/closed** system occurs when both matter and energy are exchanged between the system and the surroundings.

b Chemical equilibria can occur in **open/closed** systems.

c In some circumstances, a reversible reaction can form a **dynamic/static** equilibrium.

d The extent of reaction for chemical equilibria is **constant/different** for different equilibria.

2 Indicate whether each of the following statements about the extent of reaction is true or false.

a The extent of reaction indicates the rate of the reaction, and indicates the time taken to reach equilibrium.

b The extent of reaction is the point when there are equal amounts of reactants and products.

c The extent of reaction indicates how far the reaction has proceeded in the forward direction when equilibrium is achieved.

d The extent of reaction indicates the rate of reaction and is the point when the rate of the forward reaction is equal to the rate of the reverse reaction.

Apply

3 Hydrogen gas is mixed with iodine gas in a sealed container. A reaction occurs according to the equation:

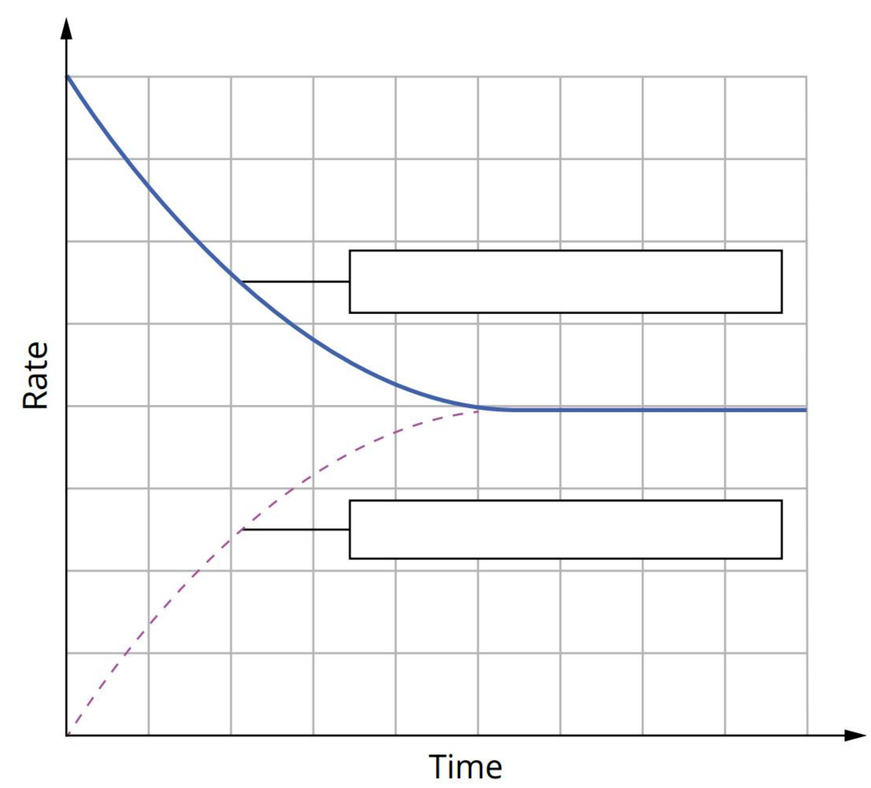
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Refer to the rate–time graph for this system shown below. Determine and label the following items on the graph.

a the forward reaction with the appropriate chemical equation

b the reverse reaction with the appropriate chemical equation

c the point when equilibrium is first established



4 Summarise dynamic equilibrium using the correct words to fill in the blanks below.

In a _____ system, as the concentrations of the reactants decrease, the rate of the forward reaction also _____. The collisions between

Continued over page

2.1 Review *continued*

these reactant molecules occur _____ frequently. Once some product starts to form, the _____ reaction occurs and the frequency of collisions between product molecules _____. At equilibrium, the rates of the forward and reverse reactions are _____ and the concentrations of all species do not change.

5 Describe the link(s) between the reversible arrow used in some chemical equations and the state of equilibrium.

Analyse

6 Classify the following systems as open or closed and explain your reasoning.

a a car engine in operation
b a can of soup
c a tree

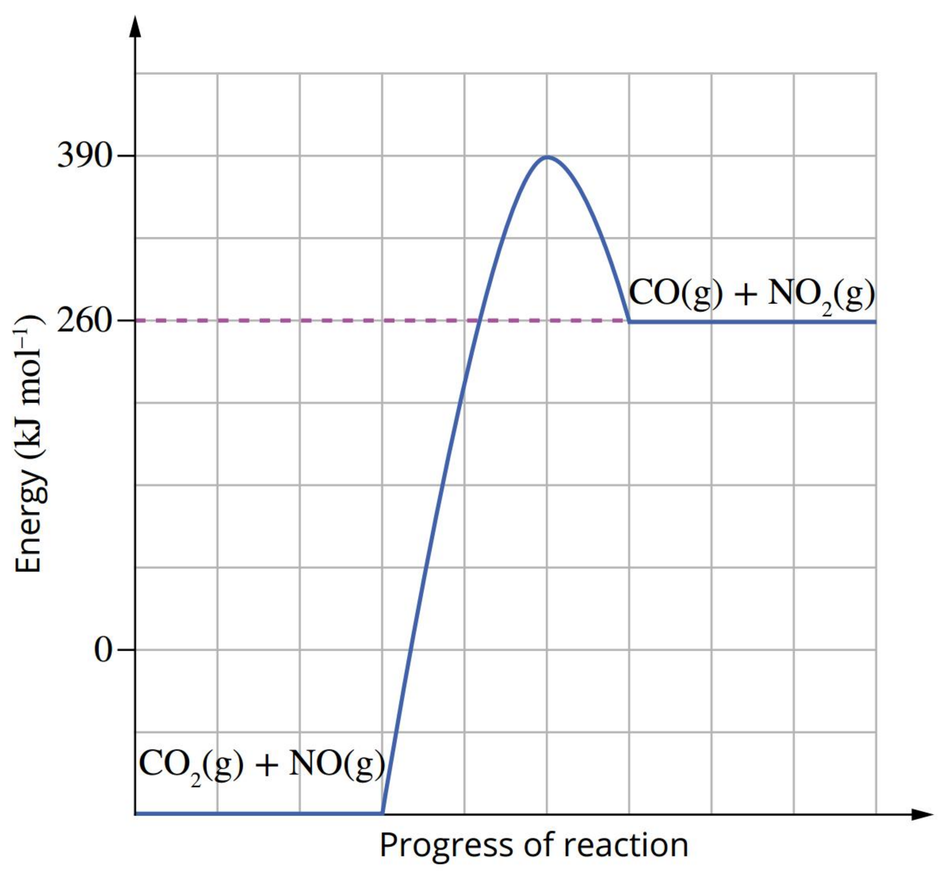
7 Determine which of the following systems are at equilibrium and explain your answer.

A a salt crystal slowly dissolving in a beaker of water
B a saturated sugar solution with sugar remaining on the bottom of the cup
C an open bottle of perfume
D the combustion of a log of wood in a campfire
E an open bottle of sparkling mineral water
F an unopened bottle of sparkling mineral water

8 The graph below shows the energy profile diagram for the reaction:

$$CO_2(g) + NO(g) \rightarrow CO(g) + NO_2(g)$$

Determine the activation energy for the reverse reaction in $kJ\,mol^{-1}$.



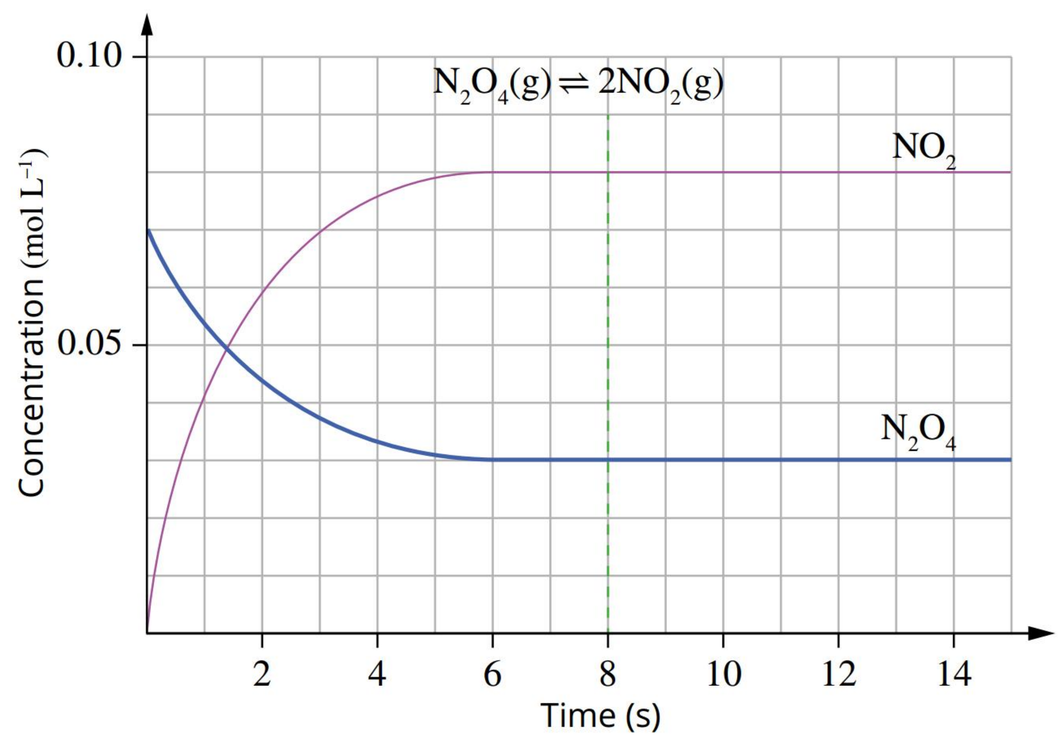
9 Consider the following equilibrium.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

a Explain what is meant by the 'dynamic nature' of equilibrium and why wet clothes in a closed laundry bag do not dry.

b When the bag in part **a** is opened, the clothes begin to dry. Assess whether this is because of an equilibrium process. Explain your answer.

10 The graph below shows the concentration versus time plot for the decomposition of dinitrogen tetraoxide: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 100°C in a 1 L reaction vessel. N_2O_4 is a colourless gas and NO_2 is brown. Use the graph to answer to the following questions.



a State the initial concentration of N_2O_4 in the flask.
b State the initial concentration of NO_2 in the flask.
c Identify the concentration of N_2O_4 at equilibrium.
d Identify the concentration of NO_2 at equilibrium.
e Calculate the number of moles of N_2O_4 that decompose during the reaction.
f State what the horizontal regions of the graph indicate.
g Identify how long it takes for equilibrium to be reached.
h Describe what a student studying this reaction will observe as the reaction proceeds.

11 Decide if the following statement is true or false and explain your reasoning. "At equilibrium the concentrations of reactants and products are equal."

2.2 Factors that affect equilibrium

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- explain the effect of adding extra reactant or product on a chemical equilibrium using collision theory and reaction rates
- predict the effect of adding extra reactant or product by the application of Le Châtelier's principle.

In this module, you will learn about how chemical systems at equilibrium are affected by changes in reaction conditions. Your understanding of the underlying principles of chemical equilibrium will enable you to predict the impact of changes when a reactant or product is added or removed from an equilibrium system, as seen in the system shown in Figure 2.2.1. In this example, the addition of excess Cl^- ions causes a net forward reaction and the solution turns blue as more $CoCl_4^{2-}$ is formed. The addition of excess water causes a net reverse reaction and the solution returns to the original pink colour as more $Co(H_2O)_6^{2+}$ is formed.

FIGURE 2.2.1 The effect of changes on the equilibrium: $Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$

You have seen in Module 2.1 that different reactions proceed to different extents. As a consequence, the relative amounts of reactants and products differ from one reaction to another at equilibrium. The relative amounts of reactants and products at equilibrium are called the **position of equilibrium**.

The relative amounts of substances present in equilibrium mixtures depend upon reaction conditions. For any equilibrium system, the position of equilibrium may be changed by:

- adding or removing a reactant or product
- changing the pressure by changing the volume of the sealed container (for equilibria involving gases)
- dilution (for equilibria in solution)
- changing the temperature.

Careful control of the reaction conditions allows chemists to maximise the equilibrium yield of a desired product by moving the position of equilibrium 'to the right', thereby increasing the amount of products formed.

LE CHÂTELIER'S PRINCIPLE

The effect of a change in reaction conditions on an equilibrium system is summarised in a useful generalisation called **Le Châtelier's principle**. The principle is named after Henri Le Châtelier (Figure 2.2.2), a French chemist and engineer.

> Le Châtelier's principle states that if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change.

When a change occurs in an equilibrium system so that it is momentarily no longer at equilibrium, the system shifts to partially counteract the effect of the change. The system will establish a new equilibrium.

As a result, the position of equilibrium will change. There may be an increase in the amount of either products or reactants, depending on the nature of the change. By understanding Le Châtelier's principle, you can predict the effect of a change to an equilibrium system. Now consider the effect of different changes on equilibrium systems.

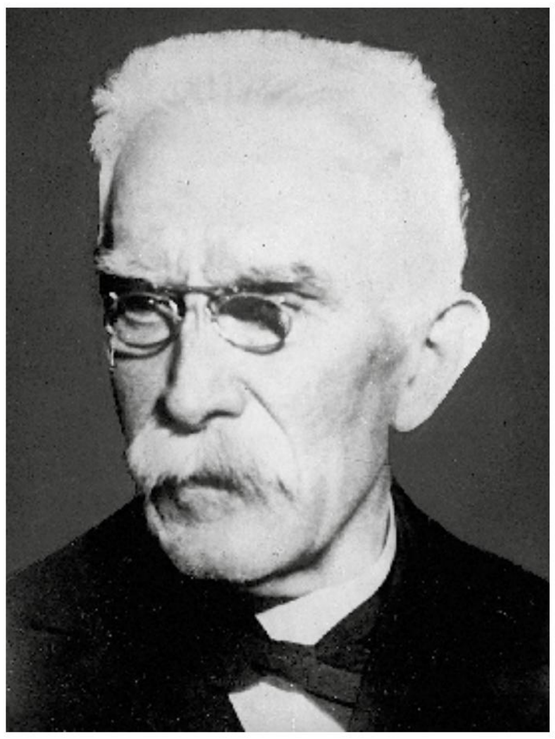


FIGURE 2.2.2 Henri Le Châtelier (1850–1936)

Adding more reactant or product

A sealed reaction vessel of nitrogen and hydrogen gases at a particular temperature will establish an equilibrium according to the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

At equilibrium, the rates of the forward and reverse reactions are equal. The concentrations of the three gases are constant. If more nitrogen gas were added to the container without changing the volume or temperature, the mixture would momentarily not be in equilibrium. The system would then adjust to form a new equilibrium with different concentrations and partial pressures of N_2, H_2 and NH_3.

You can predict the change in the position of the equilibrium by using Le Châtelier's principle. The underlying basis for this prediction can be understood by applying the principles of collision theory and rates of reactions.

Predicting the effect of a change using Le Châtelier's principle

The effect of adding the N_2 gas to the equilibrium may be predicted simply by applying Le Châtelier's principle. According to Le Châtelier's principle, if N_2 is added to an equilibrium system, the system will shift to decrease the concentration of the added N_2, so a net forward reaction will occur.

It is important to note that, even though the concentration of N_2 gas decreases as the system moves to establish the new equilibrium, its final concentration is still higher than in the original equilibrium. Le Châtelier's principle states that the change is partially opposed. The system does not return to the initial equilibrium position following the change in conditions.

> **i** Collision theory is used to explain the different rates of chemical reactions. It states that for a reaction to occur, the reactant particles must collide. The more successful collisions that occur within a specified time period, the faster is the reaction rate.

Explaining the effect of a change using collision theory and reaction rates

Instead of using Le Châtelier's principle, you can apply your knowledge of collision theory and reaction rates to understand the reasons for the effect of adding the extra N_2 gas. Because the concentration of N_2 molecules has increased, the rate of the forward reaction initially becomes greater than the rate of the reverse reaction. Then, as the concentrations of N_2 and H_2 decrease and the concentration of NH_3 increases, the rate of the forward reaction decreases and the rate of the reverse reaction increases until they become equal again. A new equilibrium is formed.

The rate–time graph in Figure 2.2.3 shows the effect on the rates of the forward and reverse reactions as the composition of the mixture adjusts to form a new equilibrium.

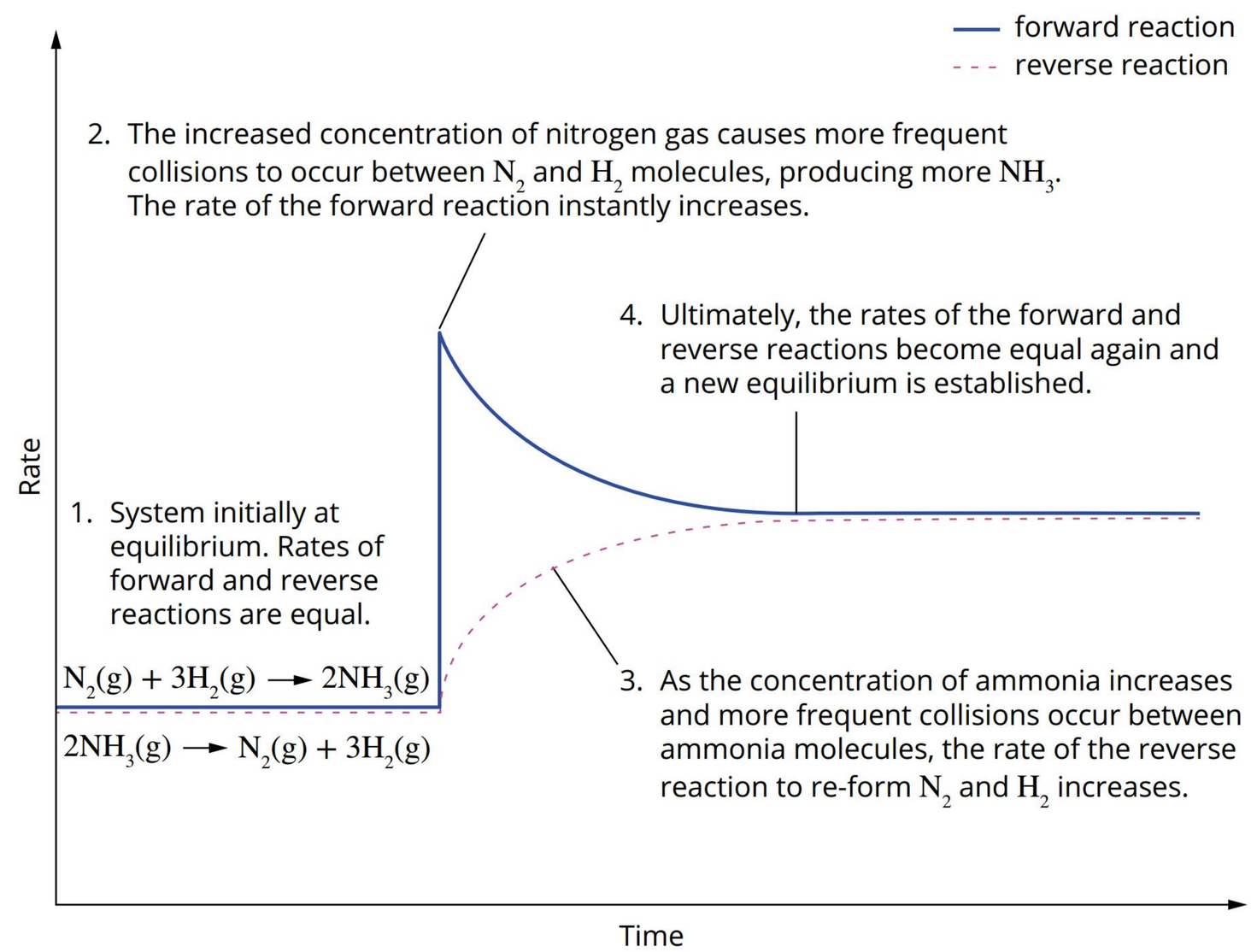


FIGURE 2.2.3 This rate–time graph shows the events that occur as a mixture of nitrogen, hydrogen and ammonia gas returns to equilibrium after the addition of extra nitrogen gas.

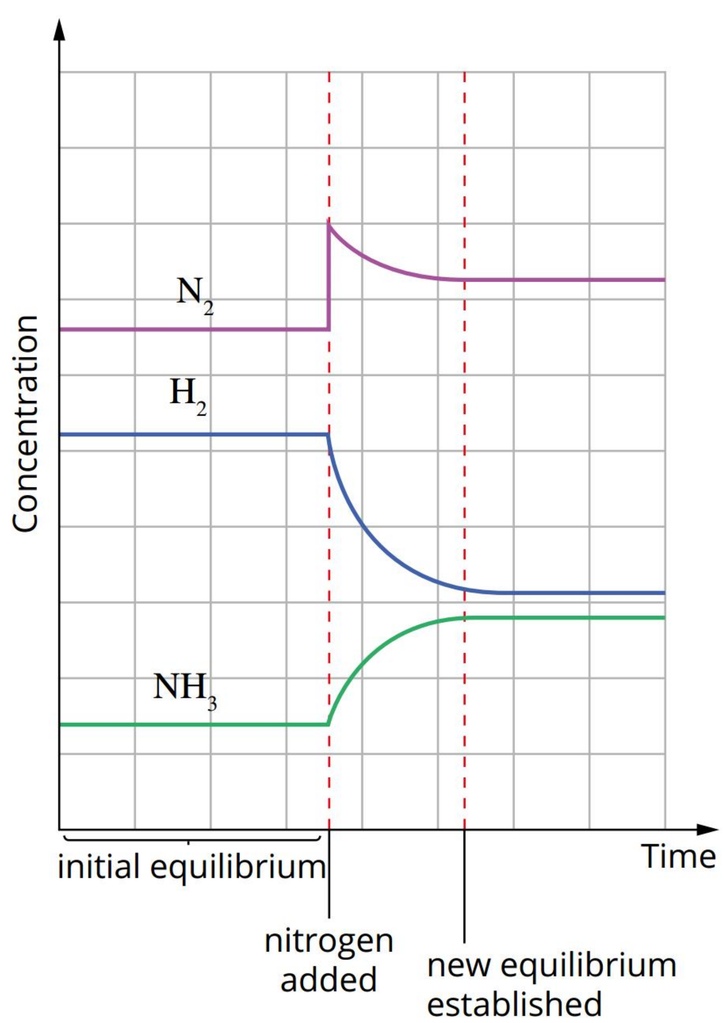


FIGURE 2.2.4 A representation of changes in concentrations that occur when additional nitrogen gas is added to the equilibrium: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Once the system has re-established equilibrium, the rates of the forward and reverse reactions will again be equal. Overall, a net forward reaction has occurred with an increase in the concentration of ammonia at equilibrium. The equilibrium position is said to have shifted 'to the right'.

The changes occurring to the system can also be shown on a concentration–time graph. Figure 2.2.4 illustrates the effect on the system when N_2 gas is added as described.

If you follow the same reasoning as for N_2, you can see that adding extra amounts of the other reactant, H_2, to the system will also increase the concentration of ammonia produced. However, the addition of more product, NH_3, would result in a net reverse reaction and the equilibrium position shifting to the left, reducing the overall concentration of ammonia, as shown in Figure 2.2.5.

While you can apply your knowledge of collision theory and reaction rates to determine the overall effect of changes on an equilibrium as was done above, applying Le Châtelier's principle is a simpler way of predicting these effects.

Table 2.2.1 summarises how an equilibrium system acts to oppose the addition or removal of reactants and products.

TABLE 2.2.1 The general effects of a change to a system at equilibrium as predicted by Le Châtelier's principle

Change to equilibrium	Effect
adding a reactant	formation of more products—a net forward reaction; equilibrium position shifts to the right
adding a product	formation of more reactants—a net reverse reaction; equilibrium position shifts to the left
removing a product	formation of more products—a net forward reaction; equilibrium position shifts to the right
removing a reactant	formation of more reactants—a net reverse reaction; equilibrium position shifts to the left

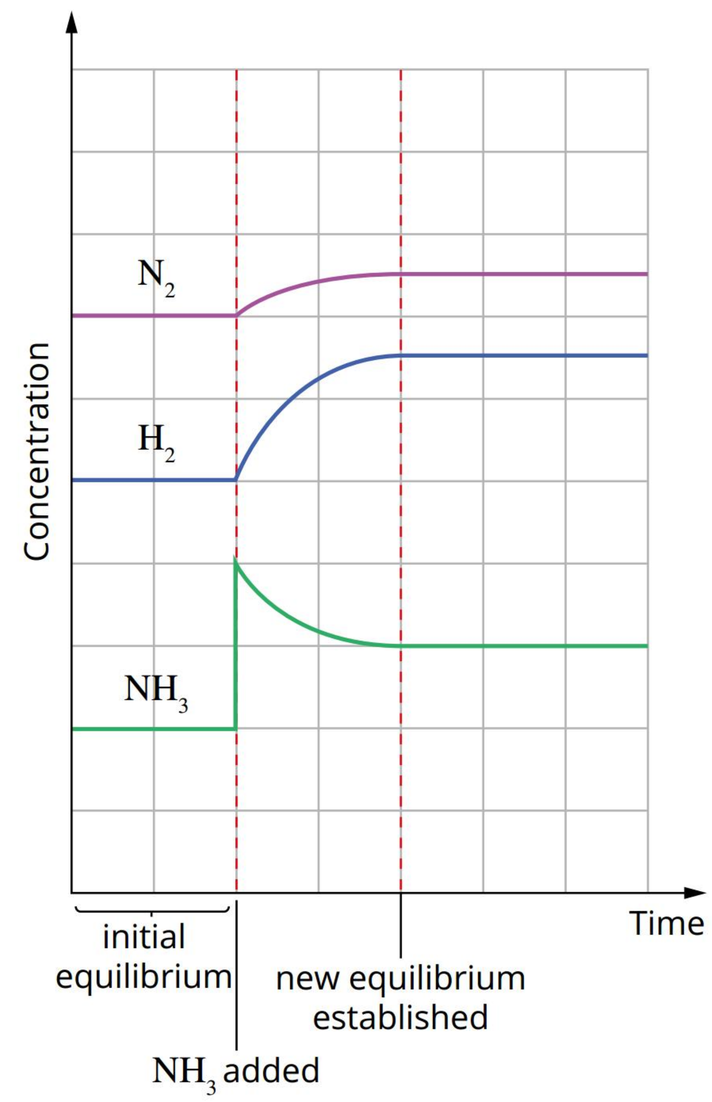


FIGURE 2.2.5 A representation of changes in concentrations that occur when additional ammonia gas is added to the equilibrium: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Worked example 2.2.1

USING COLLISION THEORY TO EXPLAIN THE EFFECT OF ADDITION OF A REACTANT OR PRODUCT ON AN EQUILIBRIUM SYSTEM

In solution, $Co(H_2O)_6^{2+}$ ions form an equilibrium with $CoCl_4^{2-}(aq)$ ions, as shown by the equation:

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

Use the concepts of rates of reaction and collision theory to predict the effect on the position of equilibrium of the addition of Cl^- ions on the equilibrium.

Thinking	Working
Determine the initial effect of the change on the concentration of the particles.	Adding Cl^- ions increases the concentration of these ions.
Use collision theory to determine the initial effect on the rate of the forward (or reverse) reaction.	Collisions between $Co(H_2O)_6^{2+}$ ions and Cl^- ions become more frequent, increasing the rate of the forward reaction and reducing the concentration of $Co(H_2O)_6^{2+}$ and Cl^- ions.
Consider how the rates of the forward and reverse reactions change as the system reaches a new equilibrium.	As more product ions, $CoCl_4^{2-}$, are formed, the rate of the reverse reaction increases, until the rates of the forward and reverse reactions become equal and a new equilibrium is established.
Predict the overall effect of the change on the position of equilibrium.	A net forward reaction has occurred and the position of equilibrium is said to have 'shifted to the right'.

➤ Try yourself 2.2.1

USING COLLISION THEORY TO EXPLAIN THE EFFECT OF ADDITION OF A REACTANT OR PRODUCT ON AN EQUILIBRIUM SYSTEM

Consider the following equilibrium system:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Use the concepts of rates of reaction and collision theory to predict the effect on the position of equilibrium of the addition of CO gas on the equilibrium.

2.2 Review

SUMMARY

- Le Châtelier's principle states that if an equilibrium system is subjected to change, the system will shift to partially oppose the change.
- The effect of a change on an equilibrium system can be predicted from Le Châtelier's principle. The effects of changes can also be explained on the basis of collision theory and reaction rates.

Change to system in equilibrium	Effect of change on equilibrium position
adding more reactant	shifts to the right (net forward reaction)
adding more product	shifts to the left (net reverse reaction)
removing some reactant	shifts to the left (net reverse reaction)
removing some product	shifts to the right (net forward reaction)

KEY QUESTIONS

Describe

1 State Le Châtelier's principle.

Apply

2 Select the correct words in the paragraph below to summarise the effect of adding additional reactant to an equilibrium system.

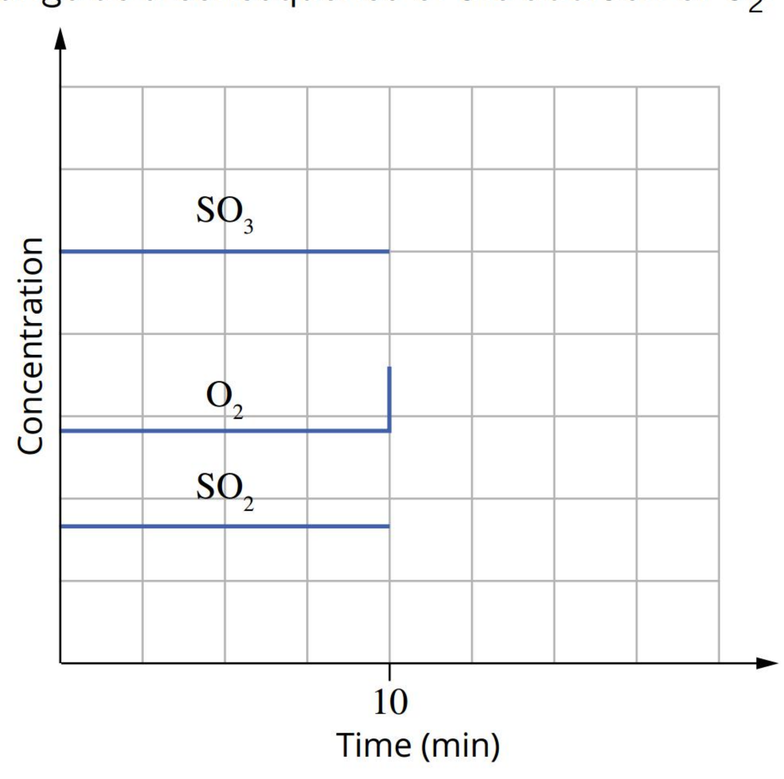
If a reactant is added to an equilibrium system, the rate of the forward reaction initially becomes **less/greater** than the rate of the reverse reaction. Then, as the concentration of reactants **increases/decreases** and the concentration of products **increases/decreases**, the rate of the forward reaction **increases/decreases** and the rate of the reverse reaction **increases/decreases** until they become equal again and a new equilibrium is formed.

3 Consider the equilibrium:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The following graph shows the concentrations of the three gases in an equilibrium mixture of constant volume and temperature. After 10 minutes, additional O_2 was added to the mixture.

Sketch a graph to show how concentrations would change as a consequence of the addition of O_2.



Analyse

4 Predict the effect of adding more hydrogen gas to the following equilibria using Le Châtelier's principle.

a $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

b $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

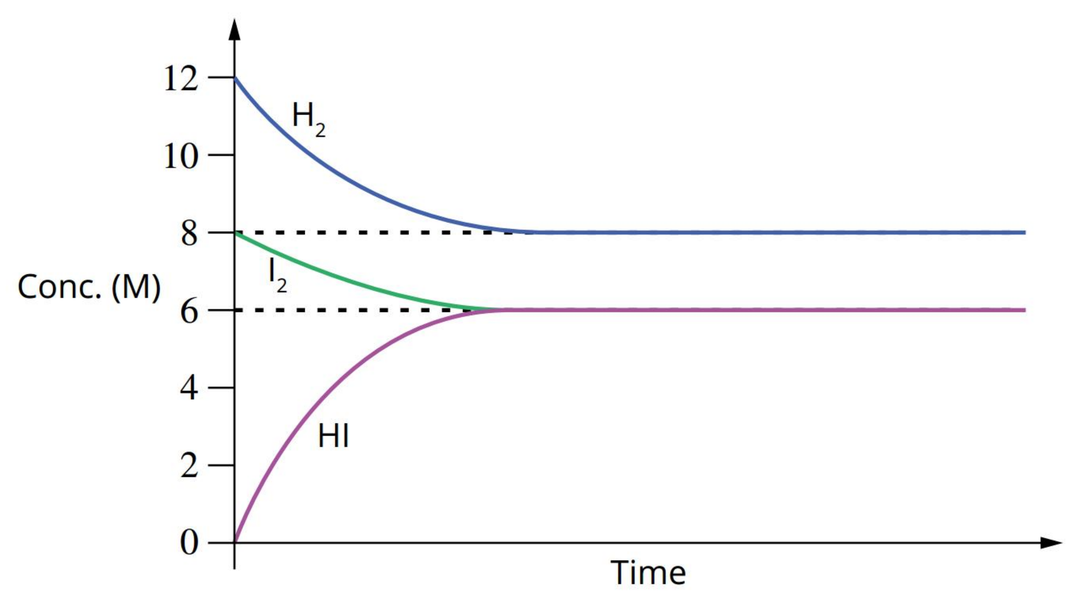
c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

5 Predict the effect of the following changes on the position of each equilibrium.

a addition of SO_3 to the equilibrium:
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

b removal of CH_3COO^- from the equilibrium:
$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

6 Identify the mole ratio error(s) in the graph showing the reaction $H_2 + I_2 \rightleftharpoons 2HI$.



2.3 Applying Le Châtelier's principle and collision theory to equilibria

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- use your knowledge of Le Châtelier's principle, collision theory and rates of reaction to predict the impact of changes in gas pressure and solution concentration on equilibria
- describe the effect of raising and lowering temperature on an equilibrium system
- explain why the presence of a catalyst does not affect the equilibrium position of a reaction.

Le Châtelier's principle can be used to understand how changes to chemical equilibria can affect numerous natural systems, as well as to optimise yields of reactions occurring in industrial processes. In the previous module, you learnt how the addition or removal of reactants and products affected the position of chemical equilibrium.

In this module, you will continue your study of the effects of changes on chemical systems at equilibrium. Your understanding of chemical equilibrium, Le Châtelier's principle, collision theory and rates of reaction will enable you to predict the impact of changes in gas pressure, solution concentration and temperature, and the addition of a catalyst on an equilibrium system.

CHANGING PRESSURE

The pressure of a gas is inversely proportional to the volume of its container. So, the pressure of gases in an equilibrium mixture can be changed by increasing or decreasing the volume of the container, while keeping the temperature constant.

Consider the effect of increasing the pressure on the equilibrium between sulfur dioxide gas, oxygen and sulfur trioxide gas for the following reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

3 gas particles 2 gas particles

You can see that the forward reaction involves a reduction in the number of gas particles from three to two. The formation of products would cause an overall reduction in pressure of the system. The reverse reaction involves an increase in the number of gas particles from two to three. So, a net reverse reaction causes an overall increase in pressure of the system.

As you saw in Module 2.2, a change in the position of an equilibrium can be predicted by applying either:

- Le Châtelier's principle, or
- an understanding of collision theory and the rates of reactions.

> Remember that gas pressure is a measure of the force per unit area, which is proportional to the number and frequency of collisions with the sides of the container. A change in the number of particles will change the pressure.

Predicting the effect of pressure change using Le Châtelier's principle

Le Châtelier's principle tells you that a system at equilibrium will respond to an increase in pressure by adjusting the position of equilibrium to reduce the pressure. Therefore, the position of equilibrium will move in the direction of the fewest gas particles.

In the example:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

an increase in pressure will cause a net forward reaction to occur to reduce the overall pressure (three gaseous reactant particles become two gaseous product particles). The amount of SO_3 present at equilibrium will increase and the position of equilibrium is said to have been shifted to the right, as shown in Figure 2.3.1.

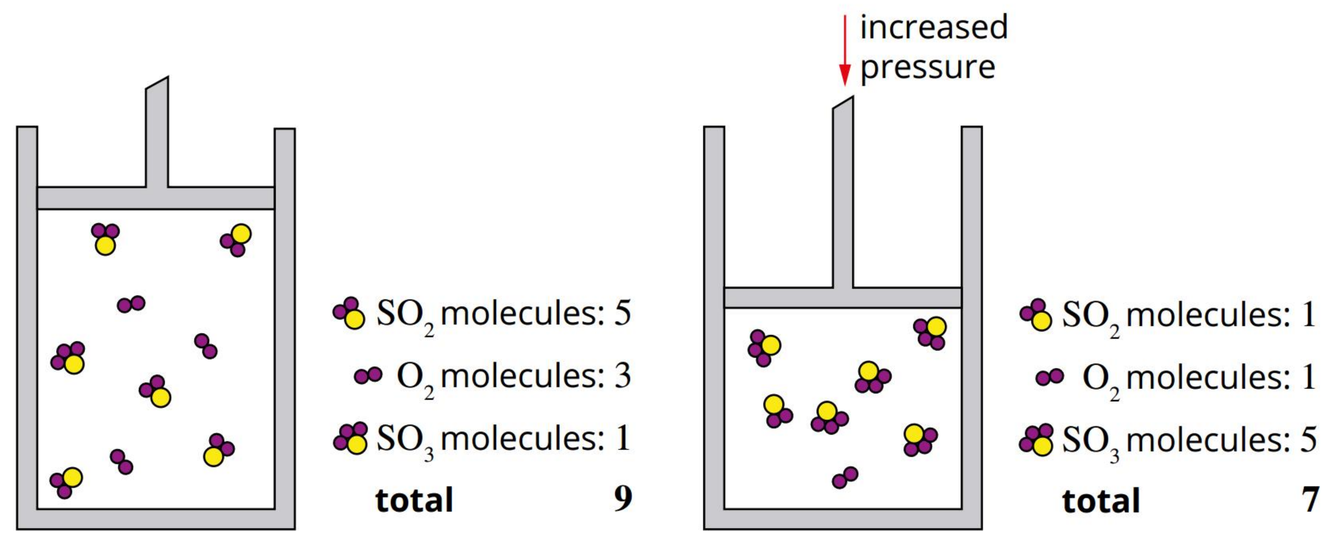


FIGURE 2.3.1 A representation of the effect of increased pressure on the equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

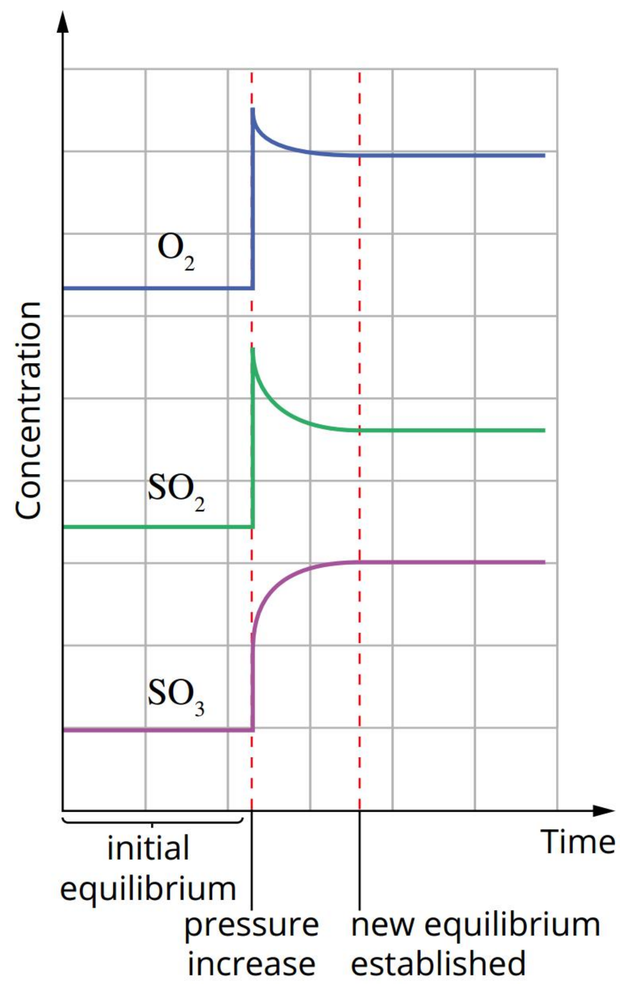


FIGURE 2.3.2 The effect of increased pressure on the equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

The effect of the change can also be illustrated graphically, as shown in Figure 2.3.2. When the system is initially at equilibrium and there is an increase in pressure, the concentrations of all gases increase simultaneously.

As the system adjusts, there is a gradual change in the concentration of each of the species until the new equilibrium is established. At the new equilibrium position, the individual concentrations are different from those at the first equilibrium.

Predicting the effect of pressure change using collision theory

The effect of a reduction in volume on the equilibrium can also be understood using collision theory. Because the overall volume occupied by the gases is smaller, the gas molecules are closer to each other and collisions between molecules become more frequent. The rate of the reaction involving the greater number of molecules (the forward reaction in this case) becomes greater than the rate of the reaction between the smaller number of molecules (the reverse reaction). Then, as more product is formed, the rate of the reverse reaction increases and the rate of the forward reaction decreases.

Eventually, the rates of the forward and reverse reactions become equal, and a new equilibrium is established. Because the forward reaction occurred to a greater extent initially, there has been a net forward reaction.

Pressure changes do not affect the equilibrium position of systems in the liquid or solid states nor for systems in aqueous solutions. Particles in these systems are too tightly packed for an increase in pressure to have a noticeable effect on volume. This means that there is negligible change in the concentration of the species involved and no effect on the position of equilibrium.

> An increase in pressure of gas particles will favour the side of the reaction with the least number of particles.

Further examples

The effect of a change of pressure or concentration, by changing the container volume, depends on the relative number of particles on both sides of the equation.

When the balanced equation shows an equal number of reactant and product particles, a change in pressure will not shift the position of equilibrium. This is the case for the reaction between hydrogen and iodine in the following equilibrium:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

2 reactant gas particles 2 product gas particles

According to Le Châtelier's principle, it does not matter which way the system shifts; the number of particles in the container will remain constant (two particles of reactants and two particles of products). Therefore, the system is unable to oppose the change applied and there is no overall net change in the position of equilibrium.

In terms of collision theory, the volume decrease causes the rates of the forward and reverse reactions to be increased equally because there are equal numbers of particles on both sides of the equation.

Worked example 2.3.1

USING LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A VOLUME DECREASE

Consider the equilibrium:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Predict the shift in equilibrium position and the effect on the amount of CO when the volume is halved at a constant temperature.

Thinking	Working
Determine the immediate effect of the change of volume on the pressure.	Halving the volume will double the pressure of all species at equilibrium.
The system will try to partially oppose the change in pressure by reducing or increasing the pressure of the system. (When there is an increase in pressure, the system will shift in the direction of the fewest gaseous particles to reduce the pressure, and vice versa when there is a decrease in pressure.) Decide how the equilibrium will respond.	There are two molecules of gas on the reactant side and four molecules of gas on the product side, so the system will shift to the left (a net reverse reaction). This decreases the amounts of the products, including CO. (Note that the CO *concentration* will still be higher than it was at the initial equilibrium position, but the *amount* will be less. The shift in equilibrium position only partially compensates for the change.)

➤ Try yourself 2.3.1

USING LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A VOLUME INCREASE

Consider the equilibrium:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

Predict the shift in equilibrium position and the effect on the amount of Cl_2 when the volume is doubled at a constant temperature.

Changing pressure by adding an inert gas

The total pressure of an equilibrium mixture of gases may also be changed, without changing the volume of the container, by adding a non-reacting gas such as helium, neon or argon. This can be seen in Figure 2.3.3.

FIGURE 2.3.3 The equilibrium of a gaseous system is unaffected by the addition of an inert gas. The total pressure of the system increases without changes in concentrations of the reactants or products.

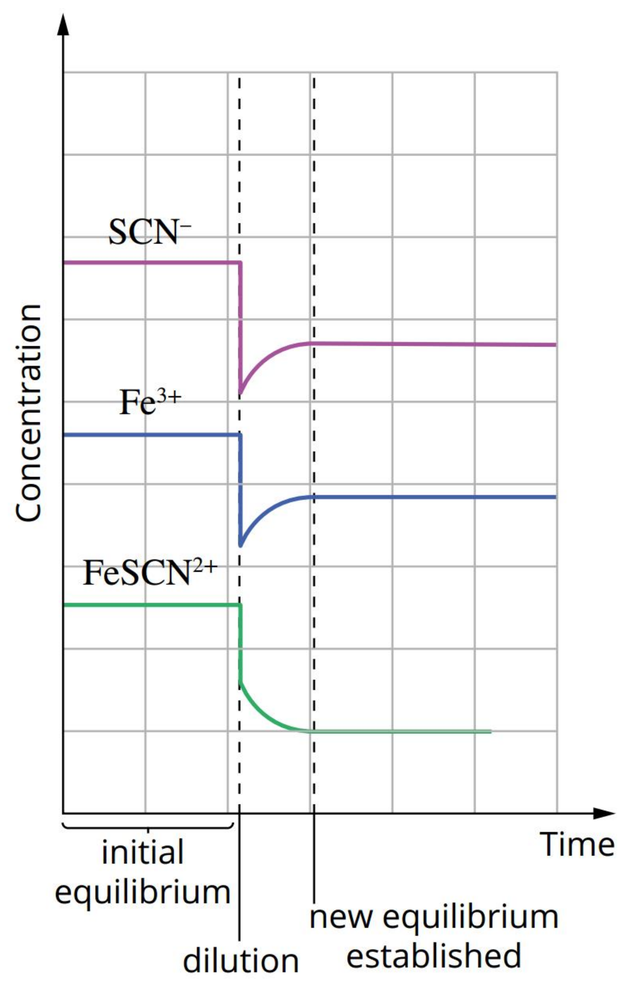


FIGURE 2.3.4 Effect of dilution on the equilibrium $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$. Although the equilibrium position shifts to the left, note that the concentrations of Fe^{3+} and SCN^{-} at the new equilibrium are lower than their concentrations prior to dilution, as the equilibrium shift only partially opposes the change.

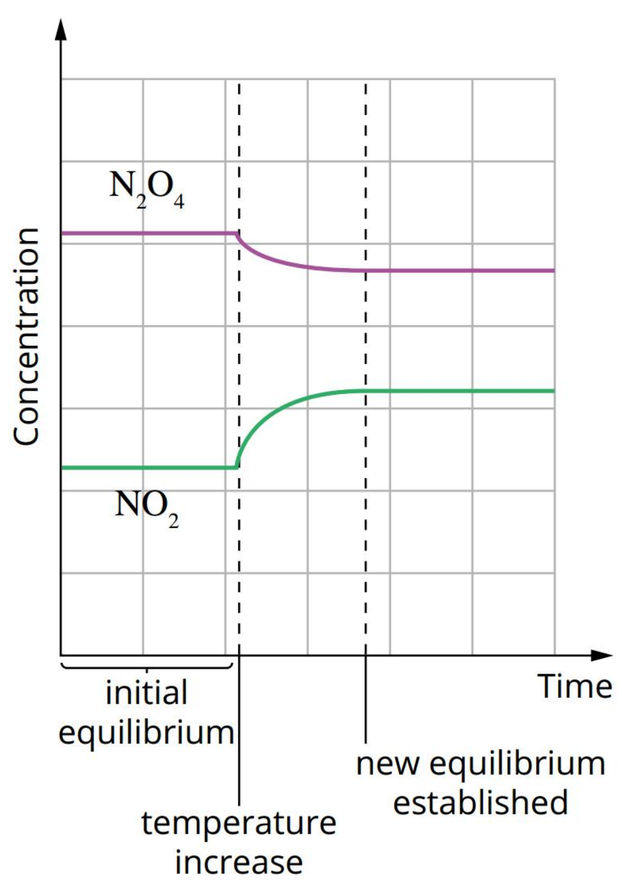


FIGURE 2.3.5 The effect of heating on the equilibrium: $2NO_2(g) \rightleftharpoons N_2O_4(g)$

Because the presence of the additional gas does not change any of the concentrations of the reactants and products, there is no effect on the position of equilibrium. Using collision theory, you can see that any collisions with inert gas molecules will not produce a reaction, so no net change in equilibrium position will be observed.

DILUTION

For equilibria in solution, the situation is similar to the one you saw with pressure and gases. The focus is on the number of particles per volume of solvent.

For an equilibrium occurring in solution, dilution by adding water reduces the number of particles per unit of volume. This results in a shift in the position of equilibrium towards the side that produces the greater number of dissolved particles.

For example, consider the equilibrium system:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

2 particles in solution 1 particle in solution

The addition of water momentarily lowers the concentration of each species. In terms of Le Châtelier's principle, a net reverse reaction will occur, increasing the total number of particles in solution – the position of equilibrium is therefore shifted to the left in this example.

Figure 2.3.4 shows the changes of concentrations that occur. Note that there is an instantaneous decrease in the concentration of all species at the time of dilution.

CHANGING TEMPERATURE

The effect of a temperature change on an equilibrium reaction depends upon whether the reaction is exothermic or endothermic. The overall effect on equilibrium position can be predicted using Le Châtelier's principle and explained using collision theory and rates of reaction.

For example, consider the conversion of brown nitrogen dioxide gas (NO_2) to colourless dinitrogen tetraoxide gas (N_2O_4). The reaction is exothermic, releasing energy to the surroundings. You could (but would not usually) write an equation for the reaction that includes the energy released:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) + \text{energy}$$

Increasing the temperature of the system increases the energy of the substances in the mixture. Applying Le Châtelier's principle, you can see that the reaction can 'oppose' an increase in energy by absorbing energy. As the reverse reaction is endothermic, this favours a net reverse reaction and the position of equilibrium will therefore shift to the left. Figure 2.3.5 shows the gradual decrease in the concentration of N_2O_4 as the system moves to produce more reactant, NO_2. Note that with a change in temperature, there is no instantaneous change in concentration.

Because the reactants and products of the system are different colours, you can monitor the change in this equilibrium visually. When a new equilibrium is attained, there is less dinitrogen tetraoxide and more nitrogen dioxide present, so the mixture appears a darker brown. This can be seen in Figure 2.3.6.

FIGURE 2.3.6 Equilibrium mixtures of NO_2 and N_2O_4 in hot water and ice. Heating the mixture favours the formation of brown NO_2 gas.

Heating an endothermic reaction causes the opposite result to occur. Applying Le Châtelier's principle, you can see that the reaction opposes an increase in energy by absorbing energy, resulting in a net forward reaction.

In summary, increasing the temperature of an equilibrium mixture results in a:

- net reverse reaction (fewer products) for exothermic reactions
- net forward reaction (more products) for endothermic reactions.

Decreasing the temperature has the opposite effect.

Predictions using Le Châtelier's principle of the effect of temperature on equilibria can be explained by collision theory. When there is an increase in temperature, molecules move faster and there are more frequent and more energetic collisions. More molecules now have the necessary energy to overcome the activation energy barrier to undergo successful collisions.

At the higher temperature, the rates of both the forward and reverse reactions increase. One of these reactions is endothermic and the other is exothermic. Because the activation energy for the endothermic reaction is greater than for the exothermic reaction, the increased energy will mean that there will be a greater proportion of molecules with the necessary energy to overcome the activation energy barrier for the endothermic reaction. The rate of this reaction will increase more than the rate of the exothermic reaction.

This can be seen from the graph in Figure 2.3.7, which shows the frequency distribution of molecules at different temperatures.

In this example of the equilibrium between NO_2 and N_2O_4, the reverse reaction is endothermic, and so there will be a net reverse reaction if the temperature increases. When the system re-establishes equilibrium at a higher temperature, the new equilibrium has a higher concentration of NO_2 and a lower concentration of N_2O_4. Conversely, decreasing the temperature of an equilibrium results in a net reaction in the direction of the exothermic reaction.

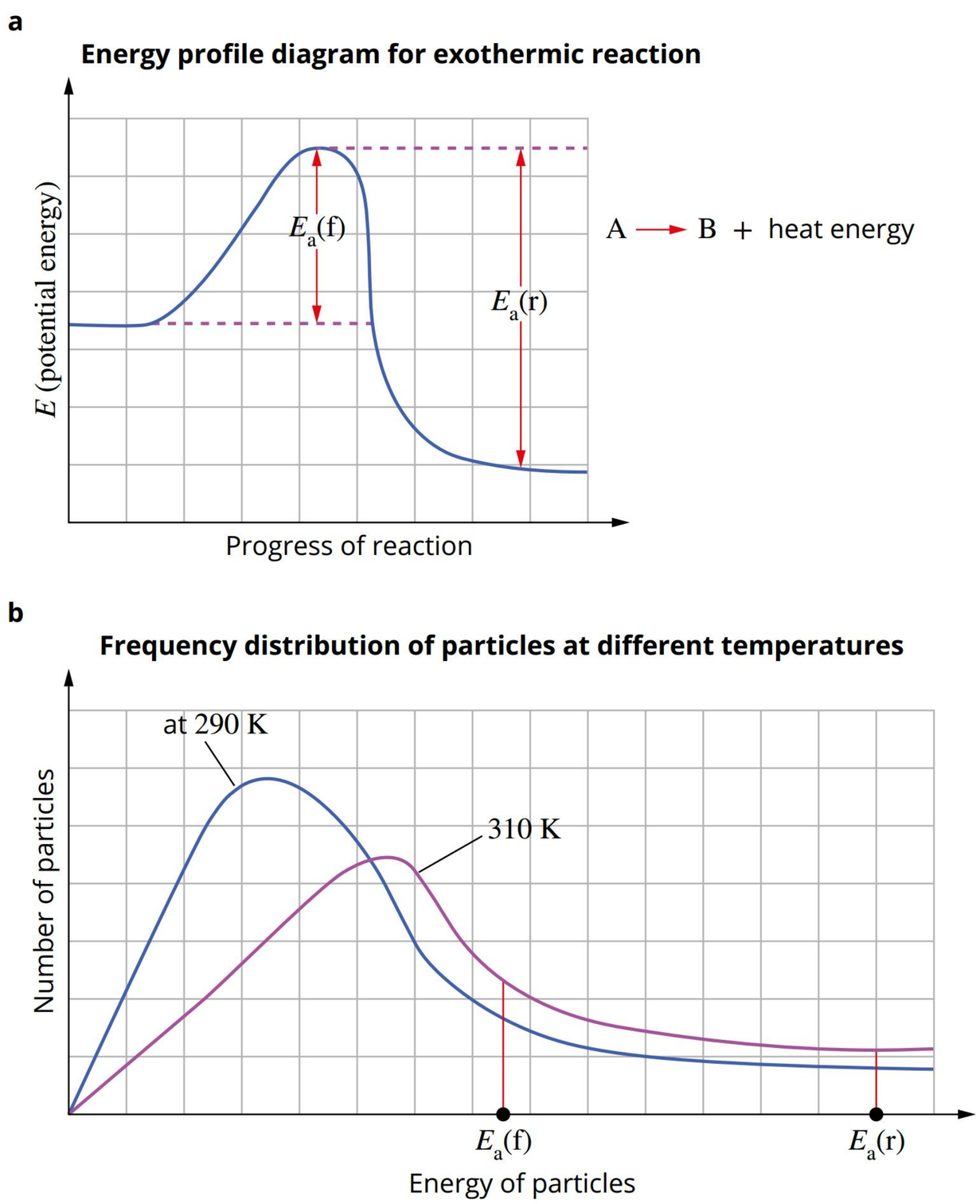


FIGURE 2.3.7 (a) An energy profile diagram for an exothermic reaction. The activation energy of the forward reaction, E_a(f), is less than the activation energy of the reverse reaction, E_a(r). (b) The frequency distribution of molecules at two different temperatures. At the higher temperature, a greater proportion of particles have the necessary energy to overcome the activation energy barrier for the endothermic reaction.

Worked example 2.3.2

USING COLLISION THEORY TO DETERMINE THE EFFECT OF TEMPERATURE ON AN EQUILIBRIUM SYSTEM

Consider the equilibrium:

$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad \Delta H = +42\,kJ\,mol^{-1}$$

Using collision theory, explain the effect of an increase in temperature on this endothermic reaction.

Thinking	Working
Decide what effect the temperature change has on the initial rates of reaction. Remember that, for an equilibrium system, an increase in temperature increases the proportion of molecules with the necessary energy to overcome the activation energy barrier for the endothermic reaction to a greater extent than for the exothermic reaction, and so the endothermic reaction will be favoured.	With the temperature increase, all reactant and product molecules have more energy and move faster. Since the forward reaction is endothermic, its rate initially increases more than the rate of the reverse reaction.
Using collision theory, consider what happens to the rates of the forward and reverse reactions.	As H_2 and CO_2 react and the concentration of reactants decreases, the rate of the forward reaction will decrease. As the concentration of CO and H_2O increases, the rate of the reverse reaction will increase. Ultimately, the rates of the forward and reverse reactions become equal, and a new equilibrium is established.
Determine the overall effect of the change on the equilibrium.	This results in a net forward reaction, with higher concentrations of the products, CO and H_2O, and lower concentrations of the reactants, CO_2 and H_2. The position of equilibrium is said to have shifted to the right.

➤ Try yourself 2.3.2

USING COLLISION THEORY TO DETERMINE THE EFFECT OF TEMPERATURE ON AN EQUILIBRIUM SYSTEM

Consider the equilibrium:

$$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) \quad \Delta H = -165\,kJ\,mol^{-1}$$

Using collision theory, explain the effect of an increase in temperature on this exothermic reaction.

EFFECT OF A CATALYST ON EQUILIBRIUM

A catalyst lowers the activation energy of the forward and reverse reactions by the same amount. This can be seen in the energy profile diagram shown in Figure 2.3.8.

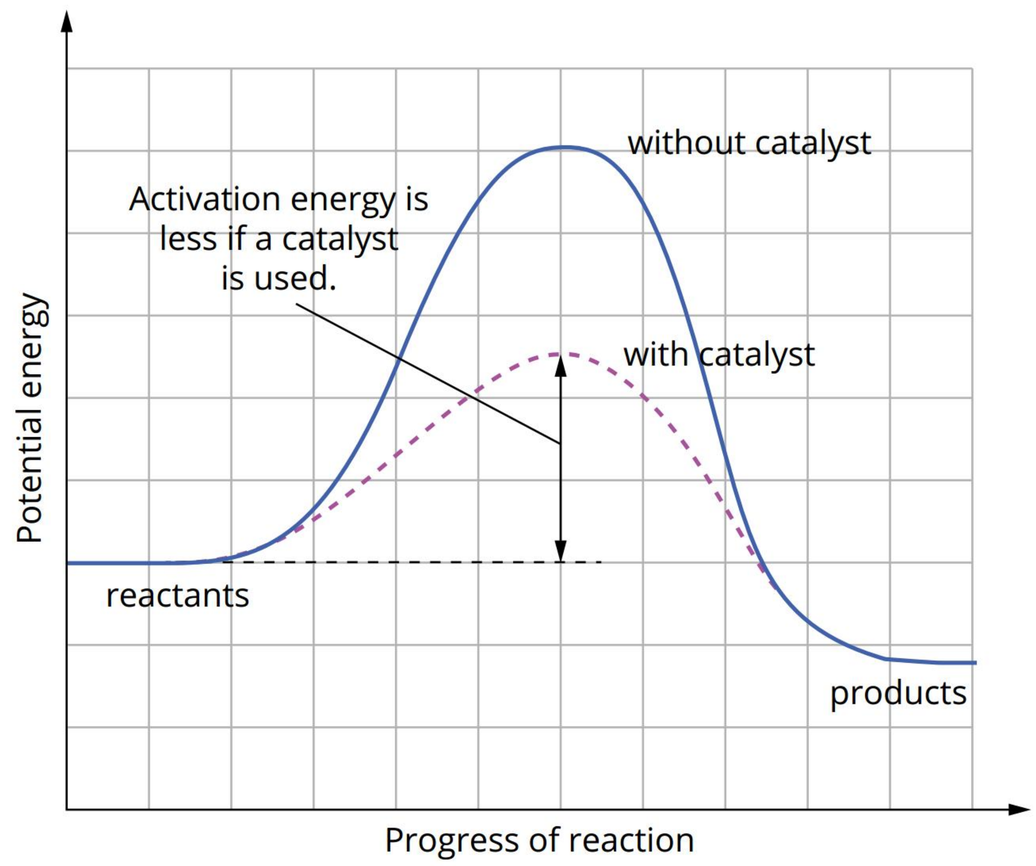


FIGURE 2.3.8 Energy changes in a catalysed and uncatalysed reaction

The lower activation energy causes an increase in the number of effective collisions. As a result, there is an increase in the rates of both forward and reverse reactions. This occurs because more particles have energies greater than the activation energy barrier of the reaction.

A catalyst increases the rates of the forward and reverse reactions equally. Therefore, it will not change the relative concentrations of the reactants and products, and the presence of a catalyst does not change the position of equilibrium. A catalyst will increase the rate at which an equilibrium is attained. It is for this reason that catalysts are used in many industrial and biological systems.

Lowering the activation energy of a reaction by the addition of a catalyst does not change the position of equilibrium of a system. Addition of a catalyst only affects how quickly equilibrium is attained.

2.3 Review

SUMMARY

- The effect of a change on an equilibrium can be predicted using Le Châtelier's principle (see table below).
- Alternatively, the effects of changes on an equilibrium can be explained on the basis of collision theory and rates of reaction (see table below).

Summary of the effect of a change on equilibrium

Change on equilibrium	Effect of change on equilibrium position	Collision theory explanation of the effect of change on equilibrium position
increasing pressure by decreasing volume (for gases)	shifts in the direction of the lower number of gas particles in the balanced chemical equation	more frequent collisions; the reaction that is more dependent on collisions (more particles reacting) occurs to a greater extent
decreasing pressure by increasing volume (for gases)	shifts in the direction of the greater number of gas particles in the balanced chemical equation	less frequent collisions; the reaction that is less dependent on collisions (fewer particles reacting) occurs to a greater extent
adding an inert gas (container volume remains constant)	no change	no change in concentration of the reacting gases, so no change to the rates of the forward and reverse reactions
adding water (dilution of solutions)	shifts in the direction of the greater number of dissolved particles in the balanced chemical equation	less frequent collisions; the reaction less dependent on collisions (fewer particles reacting) occurs to a greater extent
increasing the temperature for exothermic reactions	shifts to the left (net reverse reaction)	all reactant and product molecules have more energy and move faster; increased temperature favours the rate of an endothermic reaction; net reaction in the direction of endothermic reaction, i.e. favouring the reverse direction
increasing the temperature for endothermic reactions	shifts to the right (net forward reaction)	all reactant and product molecules have more energy and move faster; increased temperature favours the rate of an endothermic reaction; net reaction in the direction of endothermic reaction, i.e. favouring the forward direction
adding a catalyst	no change	increases rates of forward and reverse reactions to the same extent; an equivalent change in the number of successful collisions in both directions; no net reaction

KEY QUESTIONS

Describe

1 State whether the following statements are true or false.

a Adding a catalyst to an equilibrium system does not affect the position of equilibrium.

b At constant volume, increasing the temperature of an exothermic reaction at equilibrium increases the amount of products.

c At constant temperature, increasing the pressure of a gaseous equilibrium system always increases the amount of products.

d If an aqueous equilibrium system is diluted at constant temperature, the position of equilibrium shifts in the direction that produces the greater number of dissolved particles.

2 Select the correct words in this paragraph to describe the effect of adding a catalyst to an equilibrium system.

A catalyst **raises/lowers** the activation energy of a reaction and increases the rate of the forward and reverse reactions **unequally/equally**. The presence of a catalyst **does/does not** change the position of equilibrium. A catalyst **increases/does not increase** the rate at which an equilibrium is attained.

Apply

3 Summarise the effect of changes on an equilibrium system by completing the following table.

Change to equilibrium	Effect of change on equilibrium position
adding a reactant	
increasing pressure by decreasing the size of the closed container (for gases)	
adding a catalyst	
increasing the temperature for endothermic reactions	
decreasing the temperature for exothermic reactions	
adding water (dilution of solutions)	

4 The total pressure of the equilibrium system below was increased by reducing the volume at constant temperature:

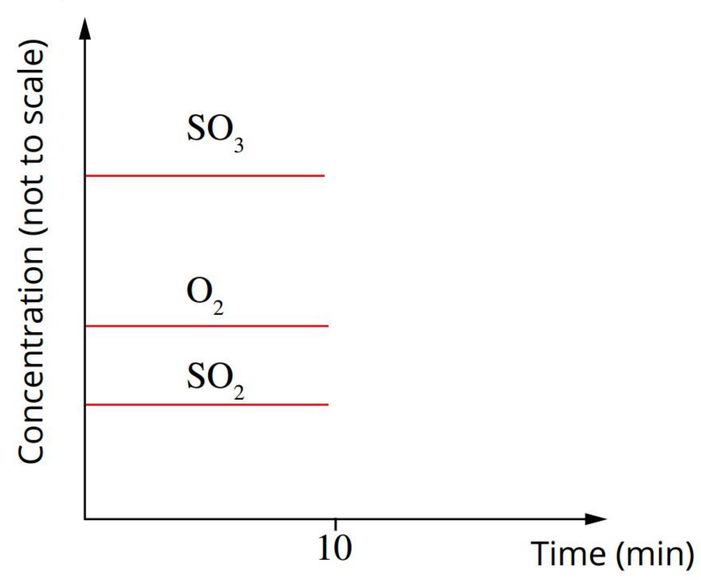
$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Explain why more N_2O_4 is formed in terms of the effect of the change on the rates of the forward and reverse reactions.

5 Consider the equilibrium:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -197\,\text{kJ mol}^{-1}$$

The graph below shows the concentrations of the three gases in an equilibrium mixture at constant volume and temperature.



Draw graphs to show how concentrations would change with time if the following changes (**a–c**) occurred separately at 10 minutes. Your graphs should show the relative stoichiometric changes in the concentration of each gas.

a The pressure of the system was suddenly increased by reducing volume.

b The temperature of the system was increased at constant volume.

c A catalyst was added at constant volume and temperature.

Analyse

6 For each of the three changes to the equilibrium system described in question **5**, predict the effect of the changes in terms of collision theory and rates of reaction.

7 Predict the effect of the following changes on the position of each equilibrium.

a halving the volume (doubling the pressure) of the equilibrium:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

b increasing the pressure of the equilibrium (by reducing volume):

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

c increasing the temperature of the endothermic equilibrium:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

8 An equilibrium mixture consists of the gases N_2O_4 and NO_2:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The volume of the container is increased at constant temperature and a new equilibrium is established. Predict how each of the following quantities would change at the new equilibrium compared with the initial equilibrium.

a concentration of NO_2

b mass of NO_2

9 Determine how the concentration of hydrogen gas in each of the following equilibrium mixtures will change when the mixtures are cooled and kept at constant volume. Explain your answer.

a $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \quad \Delta H = +138\,\text{kJ mol}^{-1}$

b $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
$\Delta H = -208\,\text{kJ mol}^{-1}$

10 The balanced equation for the reaction of hydrogen and iodine is shown.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Predict the effect that adding a catalyst would have on the reaction rate and the position of equilibrium.

11 An equilibrium is formed between two differently coloured cobalt species, $Co(H_2O)_6^{2+}(aq)$, which is pink, and $CoCl_4^{2-}(aq)$, which is blue. The equation for this equilibrium is shown.

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

When a sample of the equilibrium mixture is put into hot water, the mixture turns a deeper blue. Determine whether the forward reaction of the equation is exothermic or endothermic. Explain your reasoning.

2.4 Equilibrium constants

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that an equilibrium law expression can be written for equilibrium systems
- state equilibrium law expressions for reactions
- deduce the extent of a reaction from the value of its equilibrium constant
- solve mathematical problems using equilibrium law expressions.

In this module, you will be introduced to the equilibrium constant, K_c, and use it to investigate the relationship between the quantities of reactants and the quantities of products present when a system reaches equilibrium. The equilibrium constant allows you to:

- qualitatively predict the *relative* amounts of reactants and products in chemical equilibrium systems
- quantitatively calculate the *actual* amounts of reactants and products in chemical equilibrium systems.

Although the calculations in this section will be restricted to chemical equilibria, the same principles can be applied to other systems in our surroundings. For example, on the African plains of Tanzania, there is a delicate balance of herbivores such as zebras and wildebeest, and carnivores such as lions (Figure 2.4.1). If the populations change through drought or disease, the relative numbers change and a new balance is established. This new balance can be predicted in much the same way as occurs for chemical equilibrium.

FIGURE 2.4.1 The populations of zebras and lions in Africa can be understood using the principles of equilibrium.

INTRODUCING THE REACTION QUOTIENT, Q_c, AND THE EQUILIBRIUM CONSTANT, K_c

Consider the equilibrium system you were introduced to in Module 2.1:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

An unlimited number of different equilibrium mixtures of the three gases, nitrogen, hydrogen and ammonia, can be prepared. Table 2.4.1 shows the concentrations of each of these gases in four different equilibrium mixtures at a constant temperature of 400°C. The values of the fraction $\frac{[NH_3]^2}{[N_2][H_2]^3}$ for each mixture are also given. Note that the coefficients of the reactants and products in the chemical equation above form the indices of the reactant and product concentrations used in this fraction.

The fraction $\frac{[NH_3]^2}{[N_2][H_2]^3}$ is called the **reaction quotient** (Q_c) or **concentration fraction** of the mixture.

TABLE 2.4.1 Concentrations of reactants and products present in equilibrium mixtures

Equilibrium mixture	$[N_2]$ (mol L^{-1})	$[H_2]$ (mol L^{-1})	$[NH_3]$ (mol L^{-1})	$\frac{[NH_3]^2}{[N_2][H_2]^3}$
1	0.25	0.75	0.074	0.052
2	0.55	0.65	0.089	0.052
3	0.0025	0.0055	4.6×10^{-6}	0.051
4	0.0011	0.0011	2.7×10^{-7}	0.051

As you can see in Table 2.4.1, the reaction quotient $\frac{[NH_3]^2}{[N_2][H_2]^3}$ has an almost constant value of 0.052 for each equilibrium mixture regardless of the concentration of each component.

You can write a reaction quotient expression for any reversible chemical reaction. For example, consider the generalised equation

$$aA + bB \rightleftharpoons cC + dD$$

where a, b, c and d are the stoichiometric coefficients of substances A, B, C and D. The Q_c expression can be written as

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

In Q_c expressions, the products always appear on the top line of the expression (the numerator) and the reactants always appear on the bottom of the expression (the denominator). The terms $[A]$, $[B]$, $[C]$ and $[D]$ refer to the concentration of substances A, B, C and D, respectively. The Q_c expression is obtained by multiplying the concentration of products, divided by the concentrations of reactants, with each concentration term raised to a power equal to its stoichiometric coefficient in the balanced chemical equation.

While the reaction quotient can be calculated for any mixture of reactants and products at any time during a reaction, it is only when the mixture is at equilibrium that it gives a constant value (as in Table 2.4.1). At equilibrium, the value of the reaction quotient is equal to the **equilibrium constant**, K_c, and we can write the equilibrium law expression as

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The **equilibrium law** expression is a mathematical expression of the *law of mass action* first postulated by Norwegian scientists Cato Gulberg and Peter Waage in 1864. It asserts that for a reaction at equilibrium, and at a constant temperature, the ratio of the reactant and product concentrations has a constant value, K_c.

You will note that the expressions for Q_c and K_c take exactly the same form. However, it is important to note that when writing a K_c expression, the concentration terms refer to *equilibrium concentrations only*, whereas a Q_c expression can be written for reactant and product concentrations at any time during the reaction, *before* equilibrium is reached.

In general, for reversible chemical reactions:

- a reaction quotient expression, Q_c, can be written for reactant and product concentrations at any time during the reaction
- an equilibrium constant expression, K_c, can be written for reactant and product concentrations at equilibrium (i.e. only when the reaction has been allowed to come to equilibrium)
- different chemical reactions have different values of K_c

K_c represents the equilibrium constant for a particular reaction.

The value of K_c is different for different reactions.

K_c values are constant for a fixed temperature and will change with changes in temperature.

K_c values should therefore be reported for a particular reaction at a particular temperature.

When you write an equilibrium law expression, the concentrations of the products are always on the top of the expression.

- the size of K_c indicates the proportions (relative amounts) of reactants and products in the equilibrium mixture
- for a particular reaction, K_c is constant for all equilibrium mixtures at a fixed temperature
- K_c is temperature dependent, so the value of K_c for a particular reaction will change with changes in temperature.

A useful way of remembering the equilibrium law expression is that K_c can be represented as $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$. Remember that if there is more than one product or reactant, you must multiply the terms.

Worked example 2.4.1

WRITING AN EQUILIBRIUM LAW EXPRESSION

The decomposition of N_2O_4 is a reversible reaction that occurs according to the equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Determine the expression for the equilibrium constant K_c.

Thinking	Working
Identify the coefficients of the products and the reactants in the equation.	The product, NO_2, has a coefficient of 2 and the reactant, N_2O_4, has a coefficient of 1.
Write the expression for K_c, noting that: • the concentrations of products is written in the numerator • the concentrations of reactants is written in the denominator • each concentration term is raised to a power equal to its stoichiometric coefficient: $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$

➤ Try yourself 2.4.1

WRITING AN EQUILIBRIUM LAW EXPRESSION

Determine the equilibrium expression for K_c for the reversible reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Calculating equilibrium constants and equilibrium concentrations

An equilibrium constant, K_c, can be calculated from the molar concentrations of reactants and products at equilibrium, as shown in Worked example 2.4.2.

Worked example 2.4.2

CALCULATING AN EQUILIBRIUM CONSTANT

A 2.00 L vessel contains a mixture of 0.0860 mol of H_2, 0.124 mol of I_2 and 0.716 mol of HI in equilibrium at 460°C according to the equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Calculate the value of the equilibrium constant, K_c, at 460°C.

Thinking	Working
Find the molar concentrations for all species at equilibrium. Convert the number of moles to $mol\,L^{-1}$ using $c = \frac{n}{V}$.	The volume of the vessel = 2.00 L $[H_2] = \frac{n(H_2)}{V}$ $= \frac{0.0860}{2.00} = 0.0430\,mol\,L^{-1}$ $[I_2] = \frac{n(I_2)}{V}$ $= \frac{0.124}{2.00} = 0.0620\,mol\,L^{-1}$ $[HI] = \frac{n(HI)}{V}$ $= \frac{0.716}{2.00} = 0.358\,mol\,L^{-1}$
State the expression for K_c.	$K_c = \frac{[HI]^2}{[H_2][I_2]}$
Substitute into the expression for K_c to determine the value of K_c.	$K_c = \frac{0.358^2}{0.0430 \times 0.0620}$ $= 48.1$ Note that the there are no units for K_c (see below for an explanation).

➤ Try yourself 2.4.2

CALCULATING AN EQUILIBRIUM CONSTANT

A 3.00 L vessel contains a mixture of 0.120 mol of N_2O_4 and 0.500 mol of NO_2 in equilibrium at 460°C according to the equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Calculate the value of the equilibrium constant, K_c, at 460°C.

You can also calculate the equilibrium concentration of a reactant or product if you know the value of the equilibrium constant K_c. To do this, you will have to 'work backwards' and substitute the magnitude of K_c into the equilibrium law expression, as shown in Worked example 2.4.3.

Worked example 2.4.3

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium where $K_c = 0.400$ at 250°C:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

An equilibrium mixture contains $0.0020\,mol\,L^{-1}$ PCl_5 and $0.0010\,mol\,L^{-1}$ PCl_3 at 250°C. Determine the equilibrium concentration of Cl_2 in this mixture.

Thinking	Working
State the expression for K_c.	$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$
Substitute the known values into the expression for K_c.	$0.400 = \frac{0.0010 \times [Cl_2]}{0.0020}$
Rearrange the expression to make $[Cl_2]$ the subject of the equation and calculate the concentration of this species.	$[Cl_2] = \frac{0.400 \times 0.0020}{0.0010}$ $= 0.80\,mol\,L^{-1}$

➤ Try yourself 2.4.3

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium where $K_c = 0.720$ at 250°C:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

An equilibrium mixture contains 0.040 mol L^{-1} N_2O_4 at 250°C. Determine the equilibrium concentration of NO_2 in this mixture.

Units of K_c

You will note in the worked examples above that the values of K_c are dimensionless, even though concentration values that substitute into the equilibrium expression have the unit of molarity (M). This is because the concentration terms in the equilibrium expression are actually ratios of concentrations, referenced to a standard concentration of exactly 1 mol L^{-1}. By dividing each concentration term by 1 mol L^{-1}, the individual concentration units disappear, and we get a dimensionless K_c value.

In this text, the reference concentration of 1 mol L^{-1} will not be included in K_c expressions because it will not explicitly change the magnitude of the K_c value. Instead, we will simply use the concentration values provided, while remembering that K_c values have no units.

It is also important to note that K_c values are always positive, since we cannot have negative concentration values. Depending on the reaction, K_c values can vary over enormous ranges, typically from $\sim 10^{-30}$ up to $\sim 10^{50}$.

DEPENDENCY OF AN EQUILIBRIUM CONSTANT ON THE EQUATION

The equilibrium law expression depends upon the chemical equation used for a particular reaction.

For example, the equilibrium between the gases N_2O_4 and NO_2 can be represented by several equations. For each equation provided below, the expression for the equilibrium constant, K_c, is given. Values of K_c for this system at 25°C are also shown.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 6.2 \times 10^{-4}$$

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{6.2 \times 10^{-4}} = 1.6 \times 10^{3}$$

$$2N_2O_4(g) \rightleftharpoons 4NO_2(g) \qquad K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (6.2 \times 10^{-4})^2 = 3.8 \times 10^{-7}$$

$$\frac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g) \qquad K_c = \frac{[NO_2]}{[N_2O_4]^{\frac{1}{2}}} = (6.2 \times 10^{-4})^{\frac{1}{2}} = 2.5 \times 10^{-2}$$

You can see from these expressions that if:

- one equation is the reverse of another, the equilibrium constants are the inverse (or reciprocal) of each other
- the coefficients of an equation are doubled, the value of K_c is squared
- the coefficients of an equation are halved, the value of K_c is the square root of the original value of K_c.

Therefore, it is important to specify the equation when quoting an equilibrium constant.

> ℹ When comparing values of K_c, it is important to know the equation associated with the equilibrium constant.

INTERPRETING THE VALUE OF AN EQUILIBRIUM CONSTANT

The value of an equilibrium constant is based on the equilibrium concentrations of the products divided by the equilibrium concentrations of the reactants. Therefore, it indicates the extent of reaction at equilibrium (how far the forward reaction

proceeds before equilibrium is established) and the **equilibrium yield** (the number of moles of products present at equilibrium).

When K_c values are very large, the numerator of the equilibrium expression must be very large compared to the denominator, which means there is a relatively large amount of products compared to the amount of reactants.

When K_c values are very small, the numerator of the equilibrium expression must be very small compared to the denominator, which means there is a relatively large amount of reactants compared to the amount of products.

The relationship between the value of K_c and the relative proportions of reactants and products at equilibrium is shown in Table 2.4.2.

TABLE 2.4.2 The relationship between the value of K_c and the extent of a reaction provides information on the relative amounts of reactants and products in the reaction mixture at equilibrium.

Value of K_c	Extent of reaction
between about 10^{-4} and 10^{4}	The extent of reaction is significant. Appreciable concentrations of both reactants and products are present at equilibrium. e.g. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 0.052$ at 400°C
very large; $>10^{4}$	Almost complete reaction occurs. The concentrations of products are much higher than the concentrations of reactants at equilibrium. e.g. $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$ $K_c = 10^7$ at 25°C
very small; $<10^{-4}$	Negligible reaction occurs. The concentrations of reactants are considerably higher than the concentrations of products at equilibrium. e.g. $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ $K_c = 1.8 \times 10^{-5}$ at 25°C

Using K_c and Q_c to predict the direction of chemical reactions

You have seen that a value for the equilibrium constant, K_c, can be calculated for any chemical reaction at equilibrium. You have also noted that a value for the reaction quotient, Q_c, can be calculated for any mixture of reactants and products at any time during a reaction. For the generalised reaction

$$aA + bB \rightleftharpoons cC + dD$$

K_c is calculated using $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ and is calculated for reactions at equilibrium, while Q_c is calculated using $Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ and is calculated for reactions that have not yet reached equilibrium.

The value for K_c for a particular reaction, at a particular temperature, can only have one positive value; this is because the concentration values of all reactants and products do not change once equilibrium has been reached. By contrast, the value for Q_c can take on any positive value since the concentration values of reactants and products are changing with time up to the point at which equilibrium is established.

When $Q_c = K_c$, the reaction is at equilibrium. When $Q_c \neq K_c$, we can compare the values to determine in which direction the reaction must proceed to reach equilibrium. For example, if $Q_c > K_c$, then, relatively speaking, the numerator (or products) term is dominant compared to the equilibrium case. This means that, relatively speaking, the ratio of products to reactants is too high and the reaction will proceed to the left, consuming more products, to establish equilibrium.

By contrast, if $Q_c < K_c$, then the opposite will occur – the reaction will proceed to the right because, relatively speaking, the denominator (or reactants) term is dominant and the ratio of reactants to products is too high compared to the equilibrium case.

So, if the reaction quotient, Q_c, is:

- greater than K_c, the system 'shifts to the left' to achieve equilibrium and more reactants are formed

The concentrations used to determine K_c must be the concentration of each component of the mixture at equilibrium.

- smaller than K_c, the system 'shifts to the right' to achieve equilibrium and more products are formed
- equal to K_c, the system is at equilibrium.

The relationship between Q_c and K_c is illustrated in Figure 2.4.2. By comparing the value of Q_c for a reaction to K_c at a given temperature, it is possible to predict the direction a reaction will proceed in order to reach equilibrium.

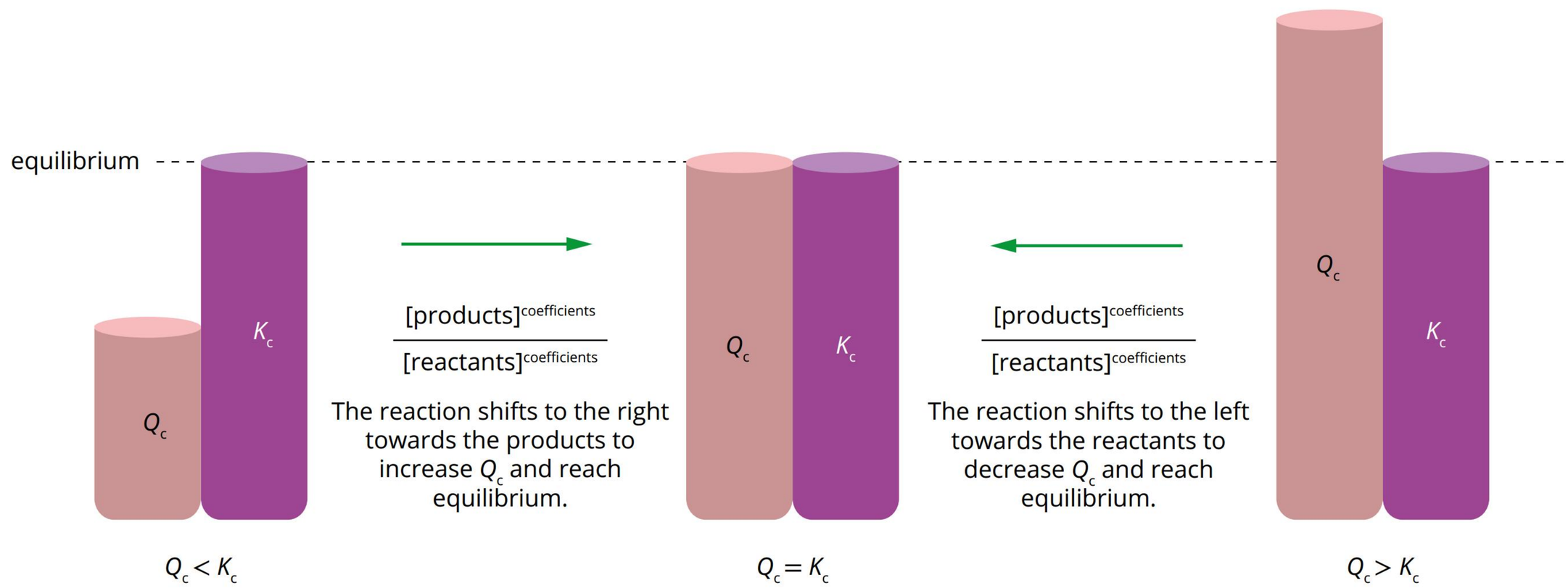


FIGURE 2.4.2 For any reversible reaction at equilibrium $K_c = Q_c$, so comparing these two values for a reaction can indicate which way a reaction must progress to reach equilibrium.

Worked example 2.4.4

PREDICTING THE DIRECTION OF A REACTION

The value of the equilibrium constant, K_c, for the following reaction is 3.07×10^{-4} at 25°C.

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

If the initial concentrations of reacting species are [NOBr] = 0.16 M, [NO] = 0.010 M and $[Br_2]$ = 0.010 M, decide in which direction the reaction will proceed.

Thinking	Working
The concentrations given are not necessarily the equilibrium concentrations. If you calculate the reaction quotient, Q_c, for concentrations given, you can then compare the value of Q_c to the value of K_c to determine which direction the reaction will proceed. Write the Q_c expression for the reaction using the general expression as a guide: $Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$	For this reaction, the Q_c expression is $Q_c = \frac{[NO]^2 [Br]}{[NOBr]^2}$ noting that the concentration terms for each substance are raised to the power indicated by the stoichiometric coefficient of each substance in the balanced chemical equation.

Substitute the given concentration values into the Q_c expression.	$Q_c = \frac{0.010^2 \times 0.010}{0.16^2}$ $= 3.9 \times 10^{-5}$
Compare the calculated Q_c value with the K_c value given in the question.	$Q_c = 3.9 \times 10^{-5}$; $K_c = 3.07 \times 10^{-4}$ Therefore, $Q_c < K_c$ and the reaction will proceed to the right.

➤ Try yourself 2.4.4

PREDICTING THE DIRECTION OF A REACTION

The value of the equilibrium constant, K_c, for the following reaction is 3.07×10^{-4} at 25°C.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

If the initial concentrations of reacting species are $[H_2] = 0.50\,M$, $[N_2] = 0.40\,M$ and $[NH_3] = 0.30\,M$, decide in which direction the reaction will proceed.

In summary, we can gain very useful information from the values of K_c and Q_c as follows:

- If $K_c >> 1$, the equilibrium mixture will be dominated by products.
- If $K_c << 1$, the equilibrium mixture will be dominated by reactants.
- If $Q_c > K_c$, the reaction will proceed to the left.
- If $Q_c = K_c$, the reaction is at equilibrium.
- If $Q_c < K_c$, the reaction will proceed to the right.

Effect of temperature on an equilibrium constant

It has been shown experimentally that the value of the equilibrium constant, K_c, for a particular reaction depends only upon temperature. It is not affected by the addition of reactants or products, changes in pressure or the use of catalysts.

As you learnt in Module 2.2, the effect of a change in temperature on reactions at equilibrium depends on whether the reaction is exothermic or endothermic. Changes in K_c values with changes in temperature also depend on whether the reaction is exothermic or endothermic. As temperature increases, for:

- exothermic reactions, the value of K_c decreases, and so the amount of products present at equilibrium decreases
- endothermic reactions, the value of K_c increases, and so the amount of products present at equilibrium increases.

Table 2.4.3 summarises the effect on K_c when temperature increases. The opposite is true when temperature decreases.

TABLE 2.4.3 The effect on the value of K_c when the temperature of a system increases

ΔH	T	K_c
exothermic (–)	increases	decreases
endothermic (+)	increases	increases

Because the value of K_c depends on temperature, it is essential to specify the temperature at which an equilibrium constant has been measured.

Only a change in temperature will change the value of K_c for a given reaction.

STOICHIOMETRIC CALCULATIONS INVOLVING THE EQUILIBRIUM CONSTANT AND CONCENTRATIONS

Calculating K_c values

K_c values can be calculated directly from the molar concentrations of reactants and products at equilibrium, as was shown in Worked example 2.4.2 on page 30. In that

An ICE table (reaction table) sets up the steps for working out equilibrium calculations where the equilibrium concentration of one or more species is unknown. The first letter of each word corresponds to the information that is recorded in each row of the table: Initial, Change, Equilibrium.

example, all equilibrium concentrations in the reaction mixture were known, making the calculation straightforward – simply substituting all concentration values into the K_c expression for the reaction given. In practice, however, it is rare to know the equilibrium concentrations of all reacting substances in an equilibrium mixture. Typically, the concentration of only one reactant or product will be monitored and measured at equilibrium.

Fortunately, this is usually sufficient, as the stoichiometric coefficients in the balanced chemical equation can be used to deduce the equilibrium concentrations of the other substances in the reaction. Once these are known, the equilibrium constant can then be calculated, as shown in Worked example 2.4.2 on page 30.

A popular way to set out calculations of this type is with the use of a **reaction table** (also known as an ICE table). The reaction table shows the *initial* amounts (or concentrations) of reactants and products, the *changes* that occur as the system reaches equilibrium and the final values at *equilibrium*, as Worked example 2.4.5 illustrates.

Worked example 2.4.5

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

An equilibrium is established between A and B at a specified temperature according to the following equation:

$$A(g) \rightleftharpoons 2B(g)$$

0.540 mol of A was placed in an empty 2.00 L vessel. When equilibrium was achieved, 0.280 mol of B was present. Calculate the value of the equilibrium constant at this temperature.

Thinking

Construct a reaction table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled 'I' (initial), 'C' (change) and 'E' (equilibrium):

	Reactants ⇌ Products	
I		
C		
E		

Enter the data provided above in the table.

When a species is consumed, the change is negative; when a species is produced, the change is positive.

Working

Initially, there is:

- 0.540 mol of A(g)
- 0.0 mol of the product B(g).

Let x mol of A react; from the coefficients of the equation $2x$ mol of B is produced.

At equilibrium, there is 0.280 mol of B(g).

	A(g) ⇌ 2B(g)	
I	0.540 mol	0.0 mol
C	$-x$ mol	$+2x$ mol
E	$0.540 - x$ mol	$2x = 0.280$ mol

Thinking

Using the coefficients from the equation, calculate the number of moles of all species at equilibrium.

Working

Initially, no B was present, so because 0.280 mol of B has been produced at equilibrium:

$2x = 0.280$ mol

$x = 0.140$ mol

We can enter these values in the table:

	A(g) ⇌ 2B(g)	
I	0.540 mol	0.0 mol
C	$-x = -0.140$ mol	$+2x = 0.280$ mol
E	$0.540 - x$ $= 0.540 - 0.140$ $= 0.400$ mol	$2x = 0.280$ mol

Using the volume of the vessel, calculate the concentrations for all species at equilibrium. Use the formula $c = \frac{n}{V}$.	The volume of the vessel is 2.00 L. $[A] = \frac{n}{V}$ $= \frac{0.400}{2.00}$ $= 0.200\,\text{mol L}^{-1}$ $[B] = \frac{n}{V}$ $= \frac{0.280}{2.00}$ $= 0.140\,\text{mol L}^{-1}$
State the expression for K_c and substitute the equilibrium concentrations. Calculate the equilibrium constant, K_c.	$K_c = \frac{[B]^2}{[A]}$ $= \frac{0.140^2}{0.200}$ $= 0.0980$

➤ Try yourself 2.4.5

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

At one step during the synthesis of nitric acid, nitrogen dioxide (NO_2) is in equilibrium with dinitrogen tetraoxide (N_2O_4) at 60°C:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

0.350 mol of N_2O_4 was placed in an empty 2.00 L vessel. When equilibrium was achieved, 0.120 mol of NO_2 was present. Calculate the value of the equilibrium constant at 60°C.

Calculations for reactions with small K_c values

If the equilibrium constant for a reaction is very low (less than about 10^{-4}), at equilibrium, the concentrations of products will be much less than the concentrations of the reactants. For reactions of this type, it is possible to calculate the concentration of the products by assuming that the equilibrium concentrations of the reactants are the same as their initial concentrations. Worked example 2.4.6 demonstrates this approach.

Although an ICE table can be used for these calculations, it is often unnecessary. Note that you must state any assumptions you make when doing calculations.

Worked example 2.4.6

CALCULATING AN EQUILIBRIUM CONCENTRATION FOR REACTIONS WITH LOW K_c

The following equilibrium has a K_c of 1.6×10^{-6} at 200°C:

$$A(g) \rightleftharpoons B(g) + C(g)$$

0.48 mol of A was placed in an empty 2.0 L vessel at 200°C. Determine the concentrations of B and C at equilibrium.

Thinking	Working
State the expression for K_c.	$K_c = \frac{[B][C]}{[A]}$

Decide if any assumptions can be made in the calculation.	Initially, there is: • 0.48 mol of A(g) • 0.0 mol of the products B(g) and C(g). From the equation, the equilibrium concentration of C will be equal to the concentration of B, i.e. [C] = [B] Since K_c is very small, the amount of reactant A converted into products will be very small, and we assume the amount of A at equilibrium is 0.48 mol. While this assumption will introduce a small amount of error to our calculations, it is a valid assumption because the number of moles of A at equilibrium can be expressed as $n_A = 0.48 - x$ ≈ 0.48 when x is very small
Calculate the concentration of the reactant.	$[A] = \frac{n}{V}$ $= \frac{0.48}{2.0}$ $= 0.24\,\text{mol L}^{-1}$
Substitute into the expression for K_c.	$1.6 \times 10^{-6} = \frac{[B][C]}{0.24}$ Since [C] = [B] $= \frac{[B] \times [B]}{0.24}$
Calculate the unknown concentration, stating the assumption you made in the calculation.	$1.6 \times 10^{-6} = \frac{[B]^2}{0.24}$ So, $3.84 \times 10^{-7} = [B]^2$ Taking the square root of both sides (use your calculator): $[B] = 6.2 \times 10^{-4}$ So, $[B] = 6.2 \times 10^{-4}\,\text{mol L}^{-1}$ and $[C] = 6.2 \times 10^{-4}\,\text{mol L}^{-1}$ Since K_c is very small, the concentration of A at equilibrium was assumed to be the same as its initial concentration.

➤ Try yourself 2.4.6

CALCULATING AN EQUILIBRIUM CONCENTRATION FOR REACTIONS WITH LOW K_c

The following equilibrium has a K_c of 4.4×10^{-8} at 200°C:

$$X(g) \rightleftharpoons 2Y(g)$$

0.30 mol of X was placed in an empty 2.0 L vessel at 200°C. Determine the concentration of Y at equilibrium.

HETEROGENEOUS EQUILIBRIA

The chemical reactions discussed so far in this module have involved **homogeneous reactions**, in which all reactants and products are in the same phase – for example, where all reactants and products exist in the gaseous state or as dissolved solutes in an aqueous solution. However, some equilibria involve **heterogeneous reactions**, in which reactants and products are in different phases.

The important feature of the equilibrium law expression for heterogeneous reactions is that the concentration of a pure solid or a pure liquid is assigned a value of 1. This is because these concentrations do not depend on how much of the pure substance is present.

Because the concentration of the solid in the heterogeneous system is considered a constant, it is removed from the equilibrium expression. As a result, the expression for the equilibrium of a heterogeneous system is often much simpler.

For example, for the equation:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

the expression for the equilibrium constant is $K_c = [CO_2]$. CaO and $CaCO_3$ are both solids and do not appear in the equilibrium law expression.

The same is true for reactions involving pure liquids. For example, the decomposition of hydrogen peroxide (H_2O_2) in the gaseous state, producing liquid water, can be represented by the following chemical equation:

$$2H_2O_2(g) \rightleftharpoons 2H_2O(l) + O_2(g)$$

Based on the balanced chemical equation, you might expect the K_c expression to be given by:

$$K_c = \frac{[H_2O]^2\,[O_2]}{[H_2O_2]}$$

However, since this is a heterogeneous equilibrium where H_2O exists in the liquid state, you omit the H_2O term. The K_c expression is therefore:

$$K_c = \frac{[O_2]}{[H_2O_2]^2}$$

For heterogeneous equilibria in solutions where the solvent is involved in the chemical reaction, its concentration can also be excluded from the equilibrium expression, provided the reactants and products are present at much lower concentrations than the solvent. In the case of *aqueous* solutions, the amount of water is extremely high compared to the amount of dissolved solute. As a result, even if water takes part in the reaction, we can exclude it from the equilibrium expression because, in effect, its concentration will not change with time, and it can be considered a pure liquid.

As an example, the reaction between the carbonate ion (CO_3^{2-}) and water (H_2O) to produce the hydrogen carbonate ion (HCO_3^-) and the hydroxide ion (OH^-) can be written as follows:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

The equilibrium expression for this equilibrium process is given by

$$K_c = \frac{[HCO_3^-]\,[OH^-]}{[CO_3^{2-}]}$$

Note how the pure liquid, H_2O, denoted with the (l), has been left out of the equilibrium expression. This approach to writing equilibrium expressions for reactions in aqueous solutions becomes very important in the next chapter where you consider equilibrium processes of weak acids and weak bases.

In summary:

- Pure liquids, pure solids and solvents are not included in the equilibrium expression.
- Only the molar concentrations of gases and molar concentrations of dissolved solutes are written into the equilibrium expression.

Worked example 2.4.7

WRITING K_c EXPRESSIONS FOR HETEROGENEOUS EQUILIBRIA

Write equilibrium expressions for the following chemical reactions.

a $2CuS(s) + 3O_2(g) \rightleftharpoons 2CuO(s) + 2SO_2(g)$

b $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

c $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

Thinking	Working
Identify the coefficients of the products and the reactants in the equation. These will be the indices of the concentration terms in the equilibrium expression. Write the expression for K_c: $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$ Only gases and dissolved substances should be included in the equilibrium expressions. Leave out pure solids, pure liquids and solvents.	**a** $K_c = \frac{[SO_2]^2}{[O_2]^3}$ **b** $K_c = \frac{[CH_3COO]}{[CH_3COOH]}$ **c** $K_c = [Pb^{2+}][I^-]^2$ or $K_{sp} = [Pb^{2+}][I^-]^2$ Note that when the equilibrium reaction involves the dissolution of a sparingly soluble salt like PbI_2, the equilibrium constant is given a special name (the solubility product) and symbol (K_{sp}). This is explained in detail in the following section.

➤ Try yourself 2.4.7

WRITING K_c EXPRESSIONS FOR HETEROGENEOUS EQUILIBRIA

Write equilibrium expressions for the following chemical reactions.

a $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

b $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$

c $Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$

Quantifying solubility: the solubility constant, K_{sp}

In part c of Worked example 2.4.7, you were shown how to determine the K_c expression for the ionic solid lead(II) iodide (PbI_2), in equilibrium with its ions in aqueous solution:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq) \quad K_c = [Pb^{2+}][I^-]^2$$

In Unit 2, you learnt that ionic compounds are generally classified as either 'soluble', 'insoluble' or 'slightly soluble' in water, with PbI_2 categorised as insoluble. While this classification suggests that 'insoluble' salts, such as PbI_2, do not dissolve in water at all, this is not entirely accurate.

Figure 2.4.3 shows the precipitation of 'insoluble' lead(II) iodide when aqueous solutions of sodium iodide and lead(II) nitrate are combined. The chemical equation for this reaction can be represented as:

$$2NaI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2NaNO_3(aq)$$

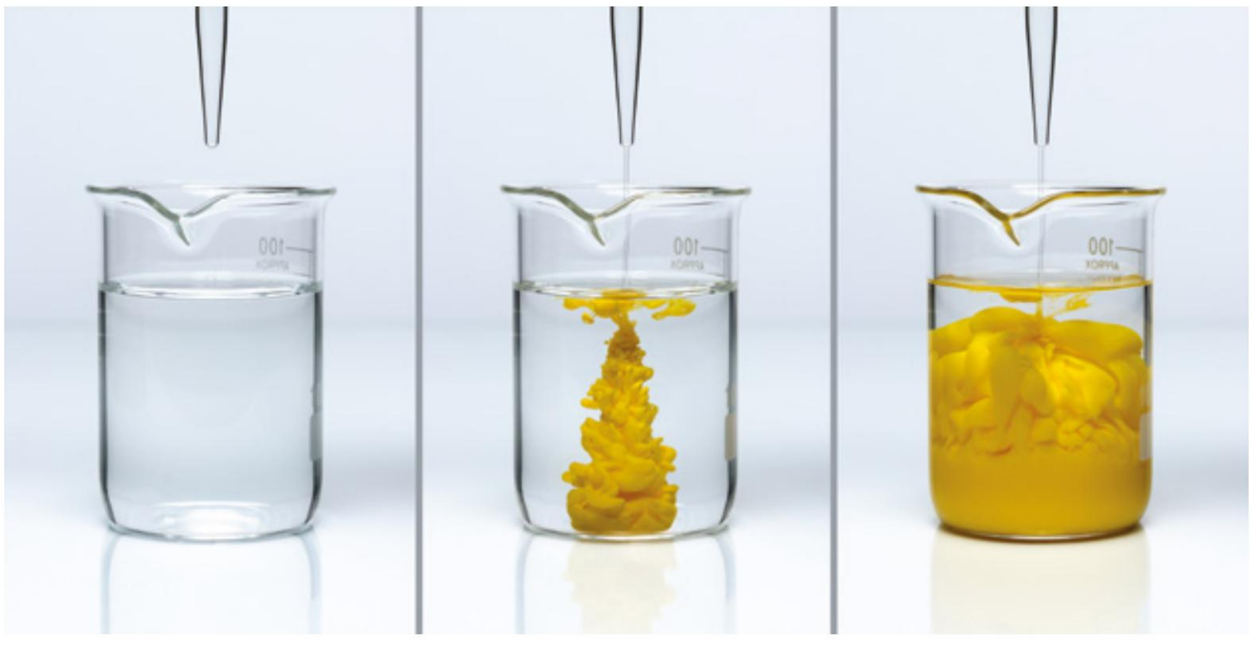


FIGURE 2.4.3 Precipitation of 'insoluble' lead(II) iodide (PbI_2) upon mixing aqueous solutions of sodium iodide (NaI) and lead(II) nitrate ($Pb(NO_3)_2$)

A close analysis of the solution after precipitation will reveal trace amounts of dissolved $Pb^{2+}(aq)$ cations and $I^-(aq)$ anions. This indicates that PbI_2, though considered insoluble, has limited solubility in water (approximately 0.056 g per 100 mL). We refer to salts that are only slightly soluble in water as **sparingly soluble salts**.

When sparingly soluble salts such as PbI_2 are added to water, they dissolve until the solution becomes saturated. At this point, a dynamic equilibrium is established between the undissolved solid and the ions in the solution. Barium sulfate ($BaSO_4$) is another example of a sparingly soluble salt, and establishes the following equilibrium when dissolved in water:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

In this saturated solution at equilibrium, the rate of dissolution of $BaSO_4$ (forward reaction) equals the rate of precipitation (backward reaction), and the concentrations of $Ba^{2+}(aq)$ and $SO_4^{2-}(aq)$ ions remain constant. Because this equilibrium describes the dissolution of a solid, the equilibrium constant is given a special name, the **solubility-constant product** (or simply the **solubility product**) with the symbol K_{sp} – where 'sp' stands for 'solubility product'. The equilibrium expression for the $BaSO_4$ equilibrium shown above is therefore written as:

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

You should note that this equilibrium process is a heterogeneous equilibrium, so the solid $BaSO_4$ term is omitted from the K_{sp} expression. You should further note that the K_c expression for the dissolution of PbI_2 written above (and in Worked example 2.4.7 on page 40) should be correctly expressed as a K_{sp} expression, i.e.:

$$K_{sp} = [Pb^{2+}]\,[I^-]^2$$

You can write a K_{sp} expression for any solid salt in equilibrium with its dissolved ions. The generalised equilibrium equation for this process can be written as:

$$aA(s) \rightleftharpoons cC(aq) + dD(aq)$$

where A(s) represents the solid, C(aq) represents the dissolved cation, D(aq) represents the dissolved anion and the lower-case a, c, and d represent the stoichiometric coefficients of substances A, C and D, respectively. The K_{sp} expression for this generalised equation is written as:

$$K_{sp} = [C]^c\,[D]^d$$

Table 2.4.4 shows balanced chemical equations and K_{sp} expressions for the dissolution of some common sparingly soluble salts. Also included are the magnitudes of the K_{sp} values for these processes at 25°C.

TABLE 2.4.4 Equilibrium equations, K_{sp} expressions and K_{sp} values for some common salts

Salt	Equilibrium equation	K_{sp} expression	K_{sp} value (25°C)
AgCl (silver chloride)	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	$K_{sp} = [Ag^+][Cl^-]$	1.77×10^{-10}
$BaSO_4$ (barium sulfate)	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$	1.08×10^{-10}
$CaCO_3$ (calcium carbonate)	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	$K_{sp} = [Ca^{2+}][CO_3^{2-}]$	3.36×10^{-9}
CuS (copper(II) sulfide)	$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$	$K_{sp} = [Cu^{2+}][S^{2-}]$	6.3×10^{-36}
FeS (iron(II) sulfide)	$FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$	$K_{sp} = [Fe^{2+}][S^{2-}]$	6.3×10^{-18}
PbI_2 (lead(II) iodide)	$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$	$K_{sp} = [Pb^{2+}][I^-]^2$	9.8×10^{-9}
ZnS (zinc sulfide)	$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$	$K_{sp} = [Zn^{2+}][S^{2-}]$	1.6×10^{-24}

Relationship between K_{sp} and solubility

The very small K_{sp} values (i.e. $K_{sp} << 1$) shown for all salts in Table 2.4.4 indicate that the position of equilibrium for each salt lies very much to the left, in favour of the solid salt rather than the dissolved ions. This is confirmation of the small extent of dissociation and the very low solubility of these salts. The sulfide salts, in particular, have extremely small K_{sp} values and are therefore considerably more 'insoluble' than the other salts listed. In this way, K_{sp} values can be used to qualitatively compare the relative solubility of sparingly soluble salts.

K_{sp} values are the mathematical product of the equilibrium concentrations of dissolved ions in water at 25°C, and they quantify the extent to which the solid dissolves. The K_{sp} value can therefore be used to quantify the solubility of sparingly soluble salts. An example of calculating the solubility of a sparingly soluble salt is shown in Worked example 2.4.8.

Worked example 2.4.8

CALUCLATING MOLAR SOLUBILITY FROM K_{sp} VALUES

Use the K_{sp} values in Table 2.4.4 to calculate the molar solubility of barium sulfate, $BaSO_4$, at 25°C.

Thinking	Working
Write the balanced chemical equation of the dissolution of $BaSO_4$. Write the K_{sp} expression and equate it to K_{sp} value from Table 2.4.4.	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ $K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$

Construct an ICE table with three rows in the table labelled 'I' (initial), 'C' (change) and 'E' (equilibrium): **Reactants ⇌ Products** I C E In this case, we note the solid reactant is irrelevant (i.e. not applicable—N/A) since the solid term does not appear in the K_{sp} expression. We therefore only need to consider the concentrations of the products.	The initial concentration of the products is zero. Let $+x$ mol L^{-1} represent the change in concentration of Ba^{2+} as the dissolution process comes to equilibrium. Since there is a 1:1 ratio between Ba^{2+} ions and SO_4^{2-} ions, the change in the concentration for SO_4^{2-} will also be $+x$ mol L^{-1}. At equilibrium, the concentrations of Ba^{2+} and SO_4^{2-} are both x mol L^{-1}. **$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$** I: N/A, 0.0 mol L^{-1}, 0.0 mol L^{-1} C: N/A, $+x$ mol L^{-1}, $+x$ mol L^{-1} E: N/A, x mol L^{-1}, x mol L^{-1}
Substitute the equilibrium concentration values into the K_{sp} expression and solve for x.	$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$ $x \times x = 1.08 \times 10^{-10}$ $x^2 = 1.08 \times 10^{-10}$ $x = \sqrt{1.08 \times 10^{-10}}$ $x = 1.04 \times 10^{-5}$ Therefore, $[Ba^{2+}] = 1.04 \times 10^{-5}$ mol L^{-1}
Determine the molar solubility.	Since Ba^{2+} and $BaSO_4$ are in a 1:1 ratio in the balanced chemical equation, the molar solubility of $BaSO_4$ is therefore 1.04×10^{-5} mol L^{-1}.

➤ Try yourself 2.4.8

CALCULATING MOLAR SOLUBILITY FROM K_{sp} VALUES

Use the K_{sp} values in Table 2.4.4 to calculate the molar solubility of lead(II) iodide PbI_2, at 25°C.

Worked example 2.4.8 shows that the K_{sp} not only describes the equilibrium behaviour of sparingly soluble salts but also enables precise quantification of their solubility.

2.4 Review

SUMMARY

- The equilibrium constant, K_c, is a constant for a particular chemical reaction at a particular temperature.
- The equilibrium law expression for the equation:

$$aA + bB \rightleftharpoons cC + dC$$

$$\text{is } K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- A reaction quotient (concentration fraction) can be calculated at any time during a chemical reaction. The reaction quotient, Q_c, has the same mathematical expression as the equilibrium law expression.
- When a reaction system at a particular temperature has reached equilibrium, the magnitude of the reaction quotient is equal to the magnitude of the equilibrium constant.
- The value of K_c provides a measure of the extent of reaction and the relative concentrations of reactants and products at equilibrium.

Value of K_c	Extent of reaction
between about 10^{-4} and 10^4	indicates significant reaction occurs
$>10^4$	indicates almost complete reaction occurs
$<10^{-4}$	indicates negligible reaction occurs

- When an equation is reversed, the new equilibrium constant is the reciprocal, or inverse, of the original K_c.
- When coefficients are doubled, K_c is squared.
- As temperature increases, the value of K_c increases for endothermic reactions and decreases for exothermic reactions.
- An equilibrium constant for a particular temperature can be calculated from the concentrations of the reactants and products at equilibrium and the expression for the equilibrium constant.
- At equilibrium, the concentration of a reactant or product can be calculated if the concentrations of the other reactants and products and the equilibrium constant are known.
- Stoichiometry may be used to calculate equilibrium concentrations of reactants and products, and hence the value of the equilibrium constant using a reaction (ICE) table.
- For heterogeneous equilibrium processes, pure liquids, pure solids and solvents are not included in the equilibrium expression – only the molar concentrations of gases and dissolved solutes are written into the equilibrium expression.
- The solubility product, K_{sp}, represents the equilibrium constant for the dissolution of a sparingly soluble ionic compound.
- The magnitude of K_{sp} can used qualitatively to compare the solubilities of sparingly soluble salts; it can also be used quantitatively to calculate the molar solubility of these salts.

KEY QUESTIONS

Describe

1 Define the following terms.

a homogeneous system

b reaction quotient

c equilibrium constant

Apply

2 Determine an expression for the reaction quotient for the reaction of hydrogen and chlorine with the equation:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

3 Determine the expression for the equilibrium constant for the following chemical equations.

a $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

b $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$

c $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$

d $4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g)$

4 A chemist investigated three different reactions and determined the value of the equilibrium constant for each. Select the reaction in which there would be substantially more products produced than reactants.

A Reaction 1: $K_c = 0.0057$

B Reaction 2: $K_c = 2.5 \times 10^9$

C Reaction 3: $K_c = 3.1 \times 10^{-3}$

Analyse

5 At a particular temperature, the equilibrium constant for the reaction represented by the following equation is 0.667:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

At a specific point in the reaction, the reaction quotient is found to be 0.234. Predict which way the reaction will shift in order to reach equilibrium with reference to the concentration of the products.

6 Consider the reaction represented by the equation:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

At 25°C, the equilibrium constant is determined to be $K_c = 0.46$. At a particular time during the reaction, the reaction quotient is 1.2.

State an expression for the reaction quotient for this reaction and predict what will happen to the system as it moves to equilibrium.

7 The equilibrium constant for the decomposition of ammonia is 100 at 255°C for the equation:

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

a State an expression for the equilibrium constant for the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

b Calculate the equilibrium constant for the equation given in part **a**.

c State an expression for the equilibrium constant for the equation:

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

d Calculate the equilibrium constant for the equation qiven in part **c**.

e Use your answers to parts **a–d** to determine the effect on the value of an equilibrium constant when the:

i equation is reversed

ii coefficients of the equation are halved.

8 Water reacts with chlorine according to the equation:

$$2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$$

At a particular temperature, the value of the equilibrium constant for this reaction is determined to be 4.0×10^{-4}. Determine the value for the equilibrium constant for the reaction if it is represented by the following equations, assuming no change in temperature.

a $H_2O(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + \frac{1}{2}O_2(g)$

b $2HCl(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g) + Cl_2(g)$

9 For the chemical reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium constant is 1.70 at 250°C.

For each equation, calculate the value of K_c at the same temperature.

a $4PCl_5(g) \rightleftharpoons 4PCl_3(g) + 4Cl_2(g)$

b $\frac{1}{2}PCl_3(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons \frac{1}{2}PCl_5(g)$

c $\frac{1}{2}PCl_5(g) \rightleftharpoons \frac{1}{2}PCl_3(g) + \frac{1}{2}Cl_2(g)$

d $2PCl_3(g) + 2Cl_2(g) \rightleftharpoons 2PCl_5(g)$

10 Predict whether the equilibrium constants for each of the following would be increased, decreased or unchanged by an increase in temperature.

a $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $\Delta H = +91\,kJ\,mol^{-1}$

b $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$ $\Delta H = -113\,kJ\,mol^{-1}$

c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\Delta H = +42\,kJ\,mol^{-1}$

d $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ $\Delta H = -564\,kJ\,mol^{-1}$

11 Calculate the equilibrium constant for the reaction represented by the equation $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, if an equilibrium mixture in a 2.0 L container was found to consist of 0.80 mol of N_2O_4 and 0.40 mol of NO_2.

12 Phosgene is a poisonous gas that was used during World War I. It can be formed by the reaction of carbon monoxide with chlorine gas in the equilibrium reaction:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

The reaction was allowed to proceed at 74°C until equilibrium was reached. The equilibrium concentrations of each species were determined and recorded as follows: $[CO] = 2.4 \times 10^{-2}\,mol\,L^{-1}$, $[Cl_2] = 0.108\,mol\,L^{-1}$ and $[COCl_2] = 0.280\,mol\,L^{-1}$. Determine the equilibrium constant for the reaction at this temperature.

13 The following reaction was allowed to reach equilibrium at a temperature of 230°C:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The value of the equilibrium constant was determined to be 6.44×10^5.

If the equilibrium concentration of $[NO_2] = 15.50\,mol\,L^{-1}$ and $[NO] = 0.0542\,mol\,L^{-1}$, determine the concentration of O_2 in the equilibrium mixture.

14 4.45 mol of PCl_3 and 5.50 mol of Cl_2 were mixed in a 2.00 L vessel. They reacted according to the equation:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

When equilibrium was reached, it was found that 0.350 mol of PCl_5 had been formed. Calculate the value of the equilibrium constant.

15 5.89 mol of N_2 and 8.23 mol of H_2 were mixed in a 5.00 L vessel. They reacted according to the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

When equilibrium was reached, it was found that 0.480 mol of NH_3 had been formed. Calculate the value of the equilibrium constant.

Continued over page

2.4 Review *continued*

16 The equilibrium constant for the following reaction is 48.8 at 455°C:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

An equilibrium mixture in a 2.00 L vessel at this temperature contains 0.220 mol of H_2 and 0.110 mol of I_2.

a Calculate the concentration of HI in this mixture.

b Another mixture was prepared by placing 4.00 mol of HI in a 2.00 L vessel at 330°C. At equilibrium, 0.440 mol of H_2 and 0.440 mol of I_2 were present. Determine the value of the equilibrium constant at this temperature.

c A third mixture consisted of 1.00 mol of HI, 0.240 mol of H_2 and 0.320 mol of I_2 in a 2.00 L container at 330°C. Deduce whether the mixture is at equilibrium and, if not, predict the direction the reaction will shift to reach equilibrium.

17 A mixture of 0.100 mol of NO, 0.051 mol of H_2 and 0.100 mol of H_2O was added to a reaction vessel with a volume of 1.00 L at 300°C. The reaction at equilibrium is given by the equation:

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

After equilibrium was established, the concentration of NO was found to be 0.062. Determine the equilibrium constant, K_c, for the reaction at 300°C.

18 The following equilibrium has a K_c of 4.4×10^{-8} at 200°C:

$$A(g) \rightleftharpoons 2B(g)$$

0.50 mol of A was placed in an empty 2.0 L vessel at 200°C. Determine the concentration of B at equilibrium.

19 Calculate the molar solubility of lead iodide (use the K_{sp} value provided in Table 2.4.4 on page 42).

20 5 mL 0.002 M $Ca(NO_3)_2$ is mixed with 5 mL 0.010 M Na_2CO_3 solution. Will a precipitate of $CaCO_3$ form?

21 1 mL 0.10 M $Ag(NO_3)$ is mixed with 4 mL 0.05 M NaCl solution. Will a precipitate form?

Chapter review

02

KEY TERMS

activation energy
catalyst
chemical energy
closed system
collision theory
concentration fraction
dynamic equilibrium
endothermic
energy profile diagram
enthalpy
equilibrium
equilibrium constant
equilibrium law
equilibrium yield
exothermic
extent of reaction
heat of reaction
heterogeneous reaction
homogeneous reaction
irreversible reaction
Le Châtelier's principle
open system
position of equilibrium
rate of reaction
reaction quotient
reaction table
reversible reaction
saturated solution
solubility-constant product
solubility product (K_{sp})
sparingly soluble salt
system
thermochemical equation

KEY QUESTIONS

Describe

1 Identify which one of the following statements about a closed system is correct.

A Energy cannot enter or leave a closed system.
B In a closed system, only products remain when the reaction is complete.
C A closed system must be completely sealed to stop reactants or products from escaping.
D In a closed system, the reactants and products cannot be exchanged with the surroundings.

2 Select which one of the following statements about a chemical equilibrium is correct.

A The reaction has stopped.
B The rate of reaction is negligible.
C The rates of the forward and reverse reactions are equal.
D At least one of the reactants has been completely consumed.

3 Hydrogen iodide formed an equilibrium with hydrogen and iodine in a sealed vessel of constant volume, according to the equation:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Additional iodine gas was added and the system was allowed to reach a new equilibrium at constant temperature. Compared to the initial equilibrium, at the new equilibrium the:

A concentration of HI would be unchanged.
B concentration of H_2 would be unchanged.
C concentration of HI would have increased.
D concentration of H_2 would have increased.

4 A closed vessel at constant temperature contains H_2 and CO_2 in equilibrium with H_2O and CO, as shown by the following equation:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \quad \Delta H = +42 \text{ kJ mol}^{-1}$$

Select which one of the following procedures will shift the equilibrium position to the right.

A addition of CO gas
B addition of a catalyst to the system
C decreasing the volume of the system
D increasing the temperature of the system

5 SO_2, O_2 and SO_3 were mixed and formed the equilibrium system:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Indicate which one of the following ratios is constant at a fixed temperature, irrespective of the initial amounts of gases.

A $\dfrac{[SO_3]}{[SO_2][O_2]}$

B $\dfrac{[SO_3]}{[SO_2]+[O_2]}$

C $\dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

D $\dfrac{[SO_2]+[O_2]}{[SO_3]}$

6 Deduce which one of the equations below has the following expression for the equilibrium constant.

$$K_c = \frac{[H_2]^2[CO]}{[CH_3OH]}$$

A $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$
B $4H_2(g) + 2CO(g) \rightleftharpoons 2CH_3OH(g)$
C $2CH_3OH(g) \rightleftharpoons 4H_2(g) + 2CO(g)$
D $CH_3OH(g) \rightleftharpoons 2H_2(g) + CO(g)$

7 Select the correct answers from the list to complete the following paragraph about equilibrium.

concentration, rates, processes, remains constant, increases, decreases, energy, matter, reversible, irreversible

Equilibrium occurs when there is a _____ reaction in a closed system. _____ can be added to the system but _____ cannot be added or removed. At equilibrium, the _____ of the forward and reverse reactions are equal. The total mass of reactants and products present in the reaction _____. There will be no observable change in the _____ of the reactants or products.

Apply

8 Determine whether the following systems are open or closed and explain your reasoning.

a a lit candle
b a refrigerator with a door that is shut
c a human being
d a weather balloon

9 Suppose CO gas and Cl_2 gas are added to a sealed container at constant temperature. A reaction occurs according to the following equation:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

Explain how equilibrium is established by sorting the following statements into the correct order.

i Equilibrium has been reached and the concentrations of CO, Cl_2 and $COCl_2$ will now remain constant.
ii When the rates of the forward and reverse reactions become equal, $COCl_2$ is formed at the same rate as it is breaking down.
iii The forward reaction will occur and, as the concentrations of CO and Cl_2 decrease, the rate of the production of $COCl_2$ decreases.
iv As $COCl_2$ is formed, some $COCl_2$ molecules decompose to re-form CO and Cl_2.

10 Use the concepts of rates of reaction and collision theory to explain the effect on the position of equilibrium of increasing the concentration of hydrogen by adding more hydrogen gas to the equilibrium system:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

11 The total pressure of the following equilibrium system was increased by reducing the volume at constant temperature:

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

Use the concepts of rates of reaction and collision theory to explain the effect on the position of equilibrium.

12 Explain the difference between the terms 'reaction quotient' (Q_c) and 'equilibrium constant' (K_c).

13 State the expression for the equilibrium constants for the following chemical equations.

a $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
b $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$
d $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Analyse

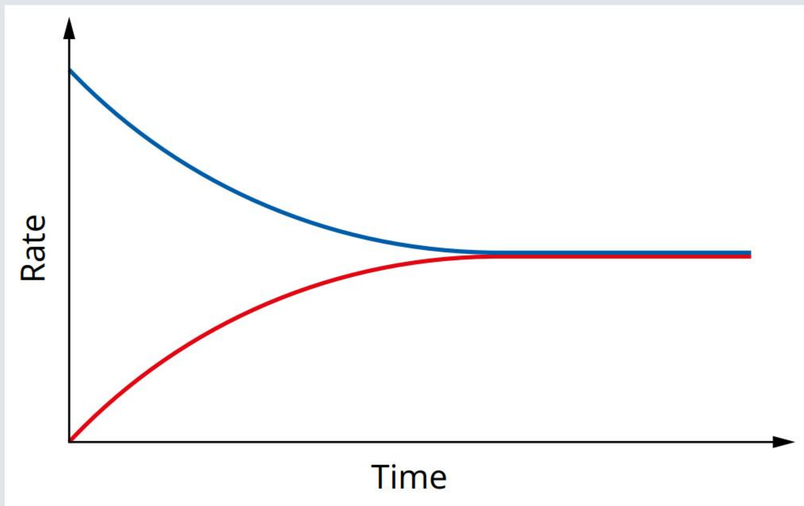
14 Determine whether the following processes occur in open or closed systems.

a a saturated solution of salt in a glass: $NaCl(s) \rightleftharpoons NaCl(aq)$
b solid $(NH_4)_2SO_4$ reacting with NaOH solution in a beaker: $(NH_4)_2SO_4(s) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2NH_3(g) + 2H_2O(l)$
c a beaker containing a solution of CH_3COOH that dissociates: $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
d burning toast

15 SO_2 and O_2 react to form an equilibrium with SO_3, according to the equation:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Analyse, using collision theory, the shape of the rate–time graph below that was obtained when SO_2 and O_2 were mixed in a container at constant temperature.



16 Elderly people, especially women, can become very susceptible to bone breakages. It is thought that as people age, they absorb Ca^{2+} from food inefficiently, reducing the concentration of these ions in body fluids. An equilibrium exists between calcium phosphate in bone and calcium ions in body fluids:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Deduce why inefficient absorption of Ca^{2+} ions could cause weakness in bones, using your understanding of equilibrium.

17 Determine in which of following reactions the position of the equilibrium is not affected by a change of volume at constant temperature, and justify your answer using collision theory.

A $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
B $Cl_2(g) + H_2(g) \rightleftharpoons 2HCl(g)$
C $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
D $2C_2H_6(g) + 7O_2(g) \rightleftharpoons 4CO_2(g) + 6H_2O(g)$

18 Predict how the concentration of hydrogen gas in each of the following equilibrium mixtures will change when the mixtures are heated and kept at constant volume.

a $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -91\,kJ\,mol^{-1}$

b $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
$\Delta H = +208\,kJ\,mol^{-1}$

19 The following equations represent reactions that are important in industrial processes. Predict the effect on the equilibrium position if each reaction mixture were compressed at constant temperature.

a $C_3H_8O(g) \rightleftharpoons C_3H_6O(g) + H_2(g)$

b $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

c $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

20 Deduce the balanced equations for the reactions with the following equilibrium equations.

a $K_c = \dfrac{[H_2]^2[CO]}{[CH_3OH]}$

b $K_c = \dfrac{[H_2S]^2}{[S_2][H_2]^2}$

c $K_c = \dfrac{[N_2O_4]^{\frac{1}{2}}}{[NO_2]}$

21 The value of K_c for the following reaction is equal to 4 at 25°C:

$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

At time *t*, the reaction quotient, Q_c, for a mixture of ethanol, water, ethyl ethanoate ($CH_3COOC_2H_5$) and ethanoic acid is equal to 6. Assuming that the mixture is also at 25°C, and, referring to the values of K_c and Q_c, predict what will happen to the concentration of ethyl ethanoate as the system reaches equilibrium.

22 Apply your knowledge about the equilibrium constant K_c to complete the following statements.

a If $K_c = 0.0001$ for a particular reaction, at equilibrium the concentrations of products will be _____ the concentrations of reactants.

b For the reaction with the equation:

$2H_2(g) + 2NO(g) \rightleftharpoons 2H_2O(g) + N_2(g)$

the expression for the equilibrium constant, K_c, is _____.

c When the reaction quotient is smaller than K_c, the reaction _____ to establish equilibrium.

23 The equilibrium constant for the following reaction at 25°C is 10^{-10}:

$2Fe^{2+}(aq) + Sn^{4+}(aq) \rightleftharpoons 2Fe^{3+}(aq) + Sn^{2+}(aq)$

a Identify whether a significant reaction would occur when solutions of tin(IV) chloride and iron(II) chloride are mixed.

b Determine the value of the equilibrium constant for the reaction:

$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$

c Explain whether a significant reaction would occur when solutions of tin(II) chloride and iron(III) chloride are mixed.

24 Consider the following equilibrium at 227°C:

$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$

a State the expression for K_c for the equilibrium system.

b Given that the value of K_c at 227°C for the expression in part **a** is 32, deduce the equilibrium constant for each of the following.

i $BrCl(g) \rightleftharpoons \frac{1}{2}Br_2(g) + \frac{1}{2}Cl_2(g)$

ii $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g)$

iii $4BrCl(g) \rightleftharpoons 2Br_2(g) + 2Cl_2(g)$

iv $\frac{1}{2}Cl_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons BrCl(g)$

25 The reaction used to manufacture ammonia is represented by the equation:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

The equilibrium constant for the reaction is 0.052 at 400°C.

A gas mixture contains 1.00 mol of N_2 gas, 1.00 mol of H_2 gas and 0.250 mol of NH_3 gas in a 1.00 L vessel at 400°C. Determine whether the mixture is at equilibrium and, if not, predict the direction it will shift to reach equilibrium.

26 An equilibrium mixture contains 0.020 mol of H_2O gas, 0.030 mol of H_2 gas, 0.040 mol of CO gas and 0.050 mol of CO_2 gas in a 2.00 L vessel. The gases react according to the equation:

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

Calculate the equilibrium constant at 900°C.

27 At a specified temperature, the reaction between solutions of Sn^{2+} and Fe^{3+} reaches equilibrium according to the equation:

$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$

a Determine the expression for K_c.

b If the equilibrium concentrations are 0.30 mol L^{-1} Fe^{3+}, 0.40 mol L^{-1} Fe^{2+}, 0.20 mol L^{-1} Sn^{4+} and 0.10 mol L^{-1} Sn^{2+} at a particular temperature, calculate the equilibrium constant at that temperature.

28 Propan-2-one (C_3H_6O) is used to remove nail polish. It can be prepared from propan-2-ol (C_3H_8O) using a copper–zinc catalyst, according to the equation:

$C_3H_8O(g) \rightleftharpoons C_3H_6O(g) + H_2(g)$

If an equilibrium mixture of these gases consists of 0.018 mol of propan-2-ol, 0.082 mol of propan-2-one and 0.082 mol of hydrogen in a 20.0 L vessel, calculate the value of the equilibrium constant.

29 Consider the equilibrium:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

A 3.00 L vessel contained 6.00 mol of PCl_3, 4.50 mol of PCl_5 and 0.900 mol of Cl_2 at equilibrium at 250°C.

a State an expression for the equilibrium constant for this reaction.

b Calculate the equilibrium constant for the reaction at 250°C.

c Another equilibrium mixture contains 0.002 mol L^{-1} of PCl_5 and 0.001 mol L^{-1} of PCl_3 at 250°C. Determine the concentration of Cl_2 in this mixture.

d Calculate the equilibrium constant at 250°C for the reaction:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

30 Consider the reaction:

$$A + 3B \rightleftharpoons 2C + D$$

Analysis of an equilibrium mixture in a 2.00 L container shows that 2.00 mol of A, 0.500 mol of B and 3.00 mol of D are present. If the equilibrium constant of the reaction is 0.024, calculate the:

a concentration of A, B and D at equilibrium

b concentration of C in the equilibrium mixture

c number of moles of C in the equilibrium mixture.

31 Carbon monoxide is used as a fuel in many industries. It reacts according to the equation:

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

In a study of this exothermic reaction, an equilibrium system is established in a closed vessel of constant volume at 1000°C.

a Predict what will happen to the equilibrium position as a result of:

i a decrease in temperature

ii the addition of a catalyst

iii the addition of more oxygen.

b Predict what will happen to the equilibrium constant as a result of each of the changes in part **a**.

c If carbon monoxide can be used as a fuel, what conclusion can you make about the magnitude of the equilibrium constant for the reaction?

32 **a** The equilibrium constant is 0.670 at a particular temperature for the reaction:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

A mixture of 0.100 mol L^{-1} of CO, 0.200 mol L^{-1} of H_2, 0.300 mol L^{-1} of CH_4 and 0.400 mol L^{-1} of H_2O is heated to this temperature. Predict whether the concentration of the following would increase, decrease or not change.

i CO

ii H_2

iii CH_4

iv H_2O

b When the temperature of the reaction mixture is increased by 10°C, the equilibrium constant for the reaction becomes 0.71. Determine what the enthalpy change of this reaction will be.

33 A step during nitric acid production is the oxidation of nitrogen oxide to nitrogen dioxide:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = -114\,kJ\,mol^{-1}$$

Nitrogen dioxide is a brown gas and nitrogen oxide and oxygen are colourless. An equilibrium mixture was prepared in a 1.0 L container at 350°C. Copy the following table, and for each of the changes listed, predict whether the reaction mixture would become darker or lighter. Give a reason for your choice.

	Colour change (lighter or darker)	**Explanation**
a The temperature is increased to 450°C at constant volume.		
b The volume of the container is increased at constant temperature.		
c A catalyst is added at constant volume and temperature.		
d More oxygen is added at constant volume and temperature.		

34 Ethene gas is produced from ethane gas in an endothermic reaction represented by the equation:

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \quad \Delta H = +138\,kJ\,mol^{-1}$$

a Predict whether the following changes will result in the equilibrium percentage yield of ethene increasing, decreasing or not changing.

i The volume is reduced at constant temperature.

ii More hydrogen gas is added at constant temperature and volume.

iii The temperature is increased at constant volume.

iv A catalyst is added.

v Argon gas is added at constant temperature and volume.

b Assess how each of the changes in part **a** will affect the rate at which the reaction achieves equilibrium.

35 The reaction used to manufacture ammonia is represented by:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The equilibrium constant for the reaction is 0.052 at 400°C.

Each of the following gas mixtures is contained in a 1.00 L vessel at 400°C. Determine whether each mixture is in equilibrium. If not, predict the direction the reaction will shift in order to reach equilibrium.

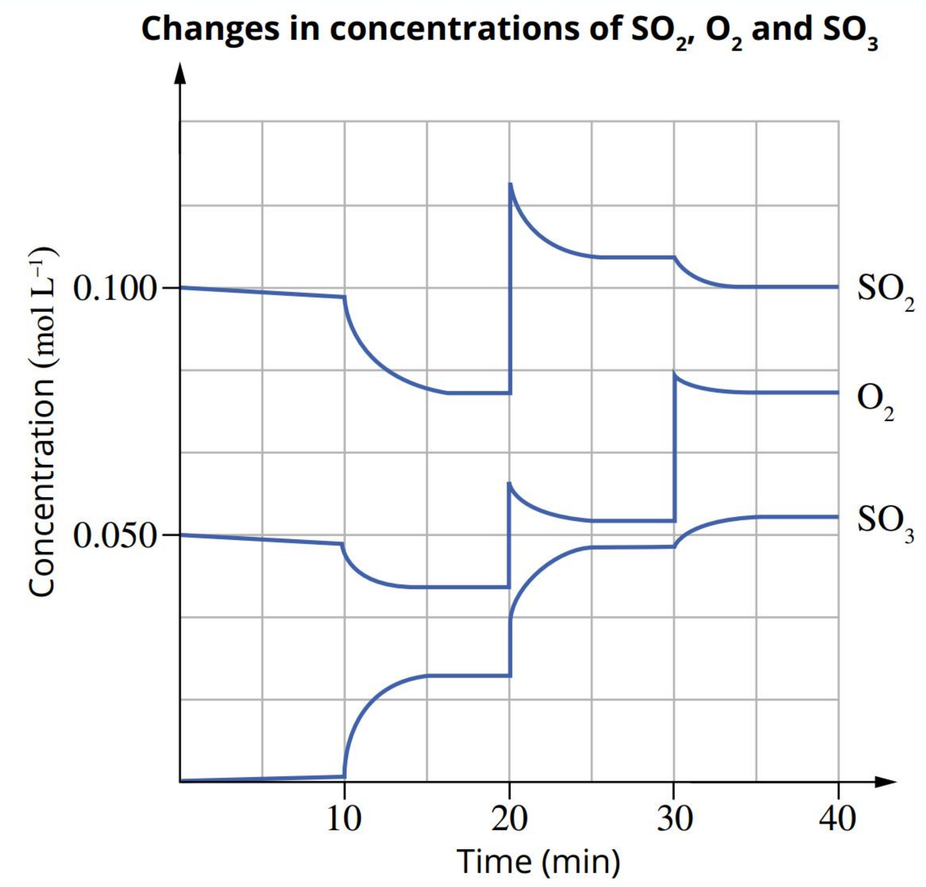
a 0.200 mol of N_2, 0.200 mol of H_2, 0.200 mol of NH_3

b 0.050 mol of N_2 and 0.500 mol of H_2

36 Sulfur dioxide gas and oxygen gas were mixed at 600°C to produce a gaseous equilibrium mixture:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

A number of changes were then made, including the addition of a catalyst, resulting in the formation of new equilibrium mixtures. The graph below shows how the concentrations of the three gases changed over time.



a State an expression for the equilibrium constant, K_c, of the reaction.

b Determine at what time intervals the reaction was at equilibrium.

c Calculate the value of K_c at 18 minutes.

d Determine at what time the was catalyst added. Explain your reasoning.

e Calculate the value of K_c at 25 minutes.

f Deduce what changes were made to the system at 20 minutes.

37 The reaction producing an ester from an alcohol and an acid occurs in the presence of an acid and is reversible. Using the word equation shown below, explain why producing an ester requires concentrated acid but the reaction conditions for the reverse reaction (hydrolysis) are dilute acid.

acid + alcohol ⇌ ester + water

38 Will a precipitate form when 1 mL of 0.0002 mol L^{-1} barium chloride is mixed with 4 mL of 0.00001 mol L^{-1} copper(II) sulfate?

Interpret

39 On occasion, a substance may be dissolved in a solution rather than water. Will a substance dissolve in seawater to the same extent as distilled water or tap water? The presence of ions already present in the aqueous solution needs to be accounted for in calculations.

Calculate the solubility of silver chloride in a 0.1 M solution of NaCl. K_{sp} for AgCl is 1.77×10^{-10}.

40 Methanol is manufactured for use as a fuel for racing cars. It can be made by the following reaction between carbon monoxide and hydrogen:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -103\,kJ\,mol^{-1}$$

a Predict what conditions of temperature and pressure would be required for a:

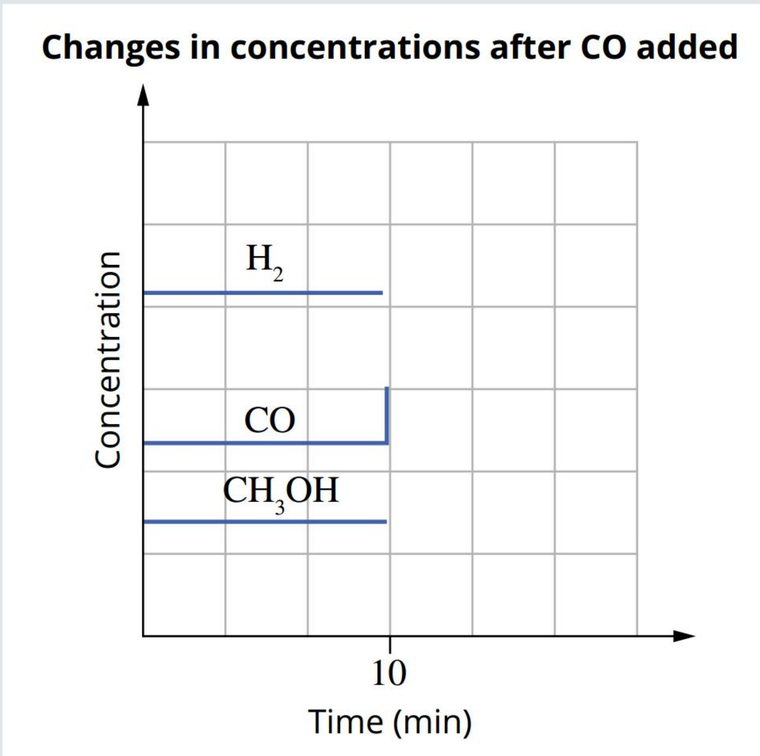
i fast reaction rate

ii high equilibrium yield of methanol.

b State whether a compromise will be needed in the choice of temperature or pressure.

c Propose another method that could be employed at a manufacturing plant to increase the rate of methanol production.

d As part of an investigation of this process, the concentration of a mixture of CO, H_2 and CH_3OH was monitored continuously. The mixture was initially at equilibrium at 400°C and constant volume. After 10 minutes, additional CO was added to the mixture, as shown in the following graph.



i Draw a graph to indicate how concentrations would change as a consequence of the addition of CO.

ii Following the addition of the CO, the mixture again reaches equilibrium. Draw a second graph to show the effect on the concentrations if the temperature was then increased to 450°C.

41 During the process for sulfuric acid manufacture, sulfur dioxide is converted to sulfur trioxide at temperatures of 400–500°C:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -197\,kJ\,mol^{-1}$$

a Predict the effect of increasing the pressure on:

i reaction rate

ii equilibrium yield.

b In practice, this step is usually performed at atmospheric pressure. Propose a reason why.

c During the process, sulfur trioxide is removed from the reaction mixture by converting it to sulfuric acid. The remaining gases are then recycled to the reaction vessel. Explain the reason for recycling the gases.

d Assess what factors would have influenced the choice of the reaction temperature.

42 Carbon disulfide gas (CS_2) is used in the manufacture of rayon. $CS_2(g)$ can be made in an endothermic gas-phase reaction between sulfur trioxide gas (SO_3) and carbon dioxide. Oxygen gas is also produced in the reaction.

a Construct a balanced chemical equation for the reaction.

b State an expression for the equilibrium constant of the reaction.

c An equilibrium mixture of these gases was made by mixing sulfur trioxide and carbon dioxide. The equilibrium mixture consisted of 0.028 mol of CS_2, 0.022 mol of SO_3, 0.014 mol of CO_2 and an unknown amount of O_2 in a 20.0 L vessel. Determine the:

i number of moles of O_2 present in the equilibrium mixture

ii value of the equilibrium constant at that temperature.

d Predict how each of the following changes to an equilibrium mixture would affect the yield of CS_2.

i removing O_2 (at constant total volume)

ii increasing the temperature

iii adding a catalyst

iv increasing the pressure by decreasing the volume of the reaction vessel (at constant temperature)

v increasing the pressure by introducing argon gas into the reaction vessel (at constant volume)

Data analysis

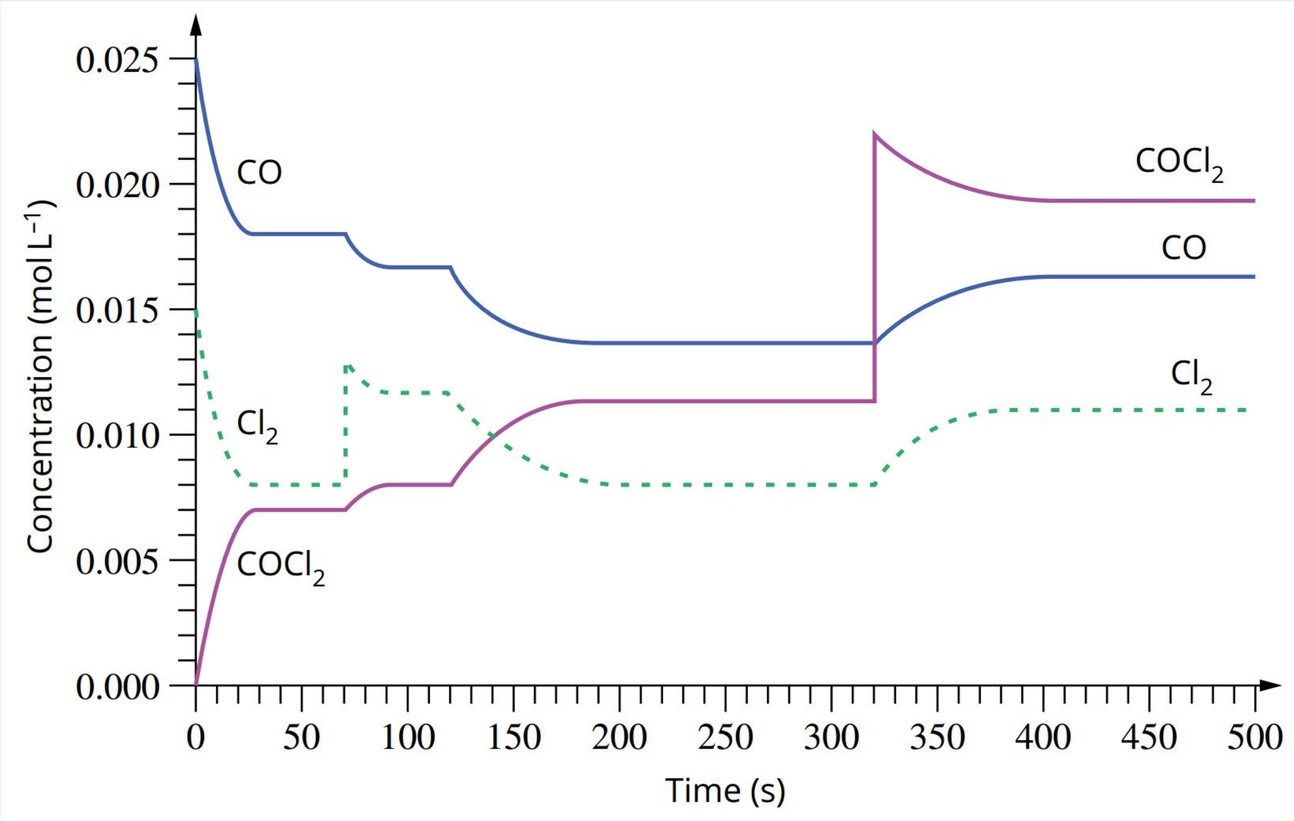
DATA SET 1

The information below applies to Questions 1–5.

The reaction between chlorine gas and carbon monoxide gas to produce phosgene is an exothermic reaction and is shown in the following equation:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

When chlorine gas and carbon monoxide gas are mixed in a closed 1.00 L container, the concentration of each species is measured during experimentation. The graph below shows this data over time.



Question 1 (1 mark)

Identify the number of times that the system establishes equilibrium between 0 and 500 seconds.

Question 2 (2 marks)

The volume of the container is increased at 500 seconds. Explain the changes occurring to concentrations as a new equilibrium is established.

Question 3 (3 marks)

Predict the change that was applied to the system at 120 seconds and describe its effect on the equilibrium constant (K_c). Show your reasoning.

Question 4 (2 marks)

Calculate K_c for the above reaction when equilibrium is first established. Show your working.

CHAPTER 03

Acid–base equilibria

Acids and bases have an important and diverse role. They are found in homes and are used extensively in industry and agriculture. Acids and bases are also the reactants and products of many chemical reactions that take place in environmental and biological systems.

In this chapter, you will study a theory that explains the characteristic reactions of acids and bases. You will also learn to represent the common reactions of acids and bases using ionic equations and investigate the distinction between strong and weak acids, and concentrated and dilute acids.

Syllabus subject matter

Topic 1 • Chemical equilibrium systems

PROPERTIES OF ACIDS AND BASES

- Identify that acids are substances that can act as proton (hydrogen ion) donors. **3.1**
- Identify acids as monoprotic, diprotic or polyprotic. **3.1**
- Identify hydrochloric, nitric and sulfuric acids as strong acids and Group 1 hydroxides and barium hydroxide as strong bases. **3.2**
- Identify carboxylic and carbonic acids as weak acids and ammonia and amines as weak bases. **3.2**
- Discriminate between the terms strong, weak, concentrated and dilute for acids and bases. **3.2**
- Discriminate between strong and weak acids and bases in terms of the extent of dissociation, rate of reaction, pH and electrical conductivity. **3.2**
- Analyse data to determine the strength, concentration, pH and electrical conductivity of acids and bases. **3.2**

PH SCALE

- Identify that water is a weak electrolyte and the self-ionisation of water is represented by K_w. (Formula: $K_w = [H^+][OH^-]$). **3.3**
- Apply K_w to calculate the concentration of hydrogen ions from the concentration of hydroxide ions in a solution. **3.3**
- Calculate pH, hydrogen ion concentration $[H^+(aq)]$, pOH and hydroxide ion concentration $[OH^-(aq)]$ for strong acids and bases. (Formula: $pH = -\log_{10}[H^+]$ and $pOH = -\log_{10}[OH^-]$). **3.3**

BRØNSTED–LOWRY MODEL

- Describe acids and bases in equilibrium systems using the Brønsted–Lowry model. **3.1**
- Explain the Brønsted–Lowry model using chemical equations that illustrate the transfer of hydrogen ions (protons) between conjugate acid–base pairs. **3.1**
- Identify that amphiprotic species can act as Brønsted–Lowry acid (or base). **3.1**
- Determine the formula of the conjugate acid (or base) of any Brønsted–Lowry base (or acid). **3.1**
- Identify that buffers are solutions that are conjugate in nature and resist a change in pH when a small amount of an acid or base is added. (Buffer calculations are not required.) **3.5**
- Apply Le Châtelier's principle to explain how buffer solutions respond to the addition of hydrogen ions and hydroxide ions. **3.5**

DISSOCIATION CONSTANTS

- Explain that the strength of acids is related to the degree of ionisation at equilibrium in aqueous solution. **3.4**
- Identify that the strength of acids can be represented with chemical equations and equilibrium constants (K_a). **3.4**
- Determine the expression for the dissociation constant for weak acids (K_a) and weak bases (K_b) from balanced chemical equations. **3.4**
- Calculate dissociation constants (K_a, K_b and K_w), pK_a, pK_b and the concentrations of reactants and products (Formula: $K_a = \frac{[H_3O^+][A^-]}{[HA]}$; $K_b = \frac{[BH^+][OH^-]}{[B]}$; $K_w = K_a \times K_b$). **3.4**
- Analyse data to compare the relative strengths of acids and bases. **3.4**

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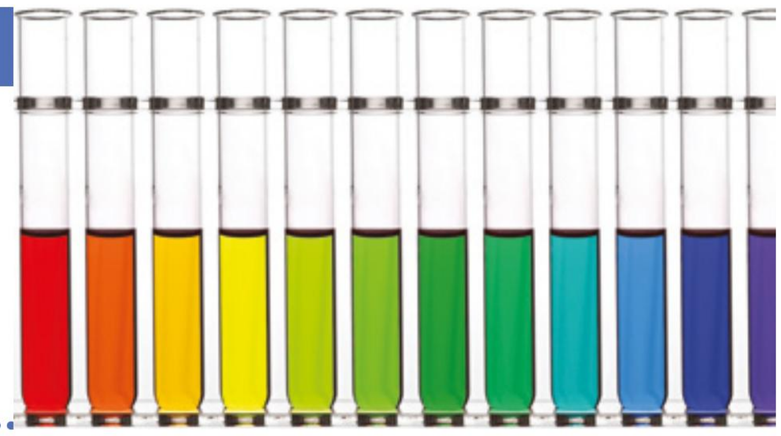
3.1 The Brønsted–Lowry model of acids and bases

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- use the Brønsted–Lowry model of acids and bases to explain how acids donate protons and bases accept these protons
- identify conjugate acid–base pairs using the Brønsted–Lowry model of acids and bases
- understand that some acids are able to donate more than one proton.



In Unit 2, you were introduced to the Arrhenius model of **acids** and **bases**. This model helps to explain why acids and bases can act as electrolytes in water. Acids form hydrogen ions and bases form **hydroxide ions**. Other properties of acids and bases are summarised in Table 3.1.1.

TABLE 3.1.1 Properties of acids and bases

Properties of acids	Properties of bases
turn litmus indicator red	turn litmus indicator blue
tend to be corrosive	are caustic and feel slippery
taste sour	taste bitter
react with bases	react with acids
solutions have a relatively low pH	solutions have a relatively high pH
solutions conduct an electric current	solutions conduct an electric current

In 1923, Danish physical chemist Johannes Nicolaus Brønsted and English chemist Thomas Martin Lowry were working independently. They each came up with the theory that now bears both of their names. The Brønsted–Lowry model is more general than the one proposed by Arrhenius and provides an explanation for some observed acid–base behaviours that cannot be explained by the earlier theories.

THE BRØNSTED–LOWRY MODEL OF ACIDS AND BASES

According to the **Brønsted–Lowry model**, a substance behaves as an acid when it donates a proton, i.e. H^+, to a base. A substance behaves as a base when it accepts a proton from an acid.

In summary:

- acids are proton donors
- bases are proton acceptors
- an **acid–base reaction** involves an exchange of protons from an acid to a base.

For example, hydrogen chloride (HCl) is a gaseous molecular compound that is very soluble in water. The molecules **ionise** in water according to the following reaction:

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

In an aqueous solution of hydrogen chloride, nearly all the hydrogen chloride is present as ions—virtually no molecules of hydrogen chloride remain. This solution is known as hydrochloric acid.

In this reaction, each HCl molecule has donated a hydrogen ion, $H^+(aq)$, to a water molecule, forming the '**hydronium ion**', $H_3O^+(aq)$. A hydrogen ion is

As you work through this chapter, you will notice that the terms 'dissociate' and 'ionise' are often used interchangeably.

While there is a subtle difference between the concepts, the syllabus does not require you to distinguish between the terms.

Dissociation is a process where a compound breaks apart into its constituent parts (normally ions); for example, when ionic NaOH(s) forms Na^+ and OH^- ions upon dissolving in water.

Ionisation is a process where ions are formed from a substance that does not initially contain ions; for example, the formation of H^+ and Cl^- ions from molecular hydrogen chloride (HCl).

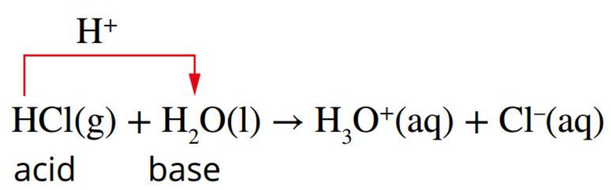


FIGURE 3.1.1 The reaction between hydrochloric acid and water is an example of an acid–base reaction, which involves a transfer of protons from an acid to a base.

essentially a proton—being a hydrogen atom that has lost its electron. Therefore, according to the Brønsted–Lowry model, HCl has acted as an acid by donating a proton to water. The water molecule has accepted a proton from the HCl molecule so, according to the Brønsted–Lowry model, water has acted as a base. This is outlined in Figure 3.1.1.

Figure 3.1.2 shows the formation of the hydronium ion by the reaction of a hydrogen ion with a water molecule. We saw in Unit 2 that the hydrogen ion and the hydronium ion are sometimes used interchangeably to represent the presence of an acidic substance in an aqueous solution. The reaction of HCl(g) with water can therefore be written in either of two ways.

a $HCl(g) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$

or

$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

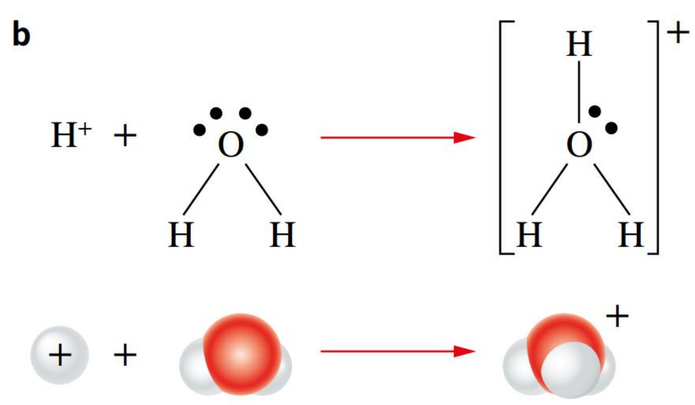


FIGURE 3.1.2 (a) Two ways to write the reaction of HCl(g) with water. (b) Formation of the hydrogen ion.

However, writing the hydrogen ion as $H^+(aq)$ in an equation makes it harder to see that an acid–base proton transfer reaction has occurred. As a result, in this chapter, the H^+ ion will usually be represented as the H_3O^+ ion, with H_2O written as a reactant (or product) in the acid–base reaction.

Advantages of the Brønsted–Lowry model

Acid–base reactions are not restricted to aqueous solutions. A reaction between two gases can be an acid–base reaction. For example, the **salt** ammonium chloride can be formed by a reaction between:

- solutions of hydrochloric acid and ammonia:

$$HCl(aq) + NH_3(aq) \rightarrow Cl^-(aq) + NH_4^+(aq)$$

- gaseous hydrogen chloride and gaseous ammonia:

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

The Brønsted–Lowry model classifies both of these reactions as acid–base reactions because in each case the acid (HCl) donates a proton to the base (NH_3).

The Brønsted–Lowry model vs the Arrhenius model

Some important concepts that arise out of the Brønsted–Lowry theory of acids and bases are summarised below:

- All Arrhenius acids and bases are Brønsted–Lowry acids and bases. However, the reverse is not true; not all Brønsted–Lowry acids and bases are Arrhenius acids and bases.
- Any process involving a Brønsted–Lowry acid must also involve a Brønsted–Lowry base. An acid and a base always work together in a proton transfer process, and you cannot have one without the other. This will become clearer in the following section when you are introduced to **conjugate acid–base pairs**.
- To be a Brønsted–Lowry acid, a molecule or ion must have a hydrogen atom that it can readily lose (donate) as an H^+ ion.
- To be a Brønsted–Lowry base, a molecule or ion must have a non-bonding (or lone) pair of electrons capable of binding (accepting) the H^+ ion in the form of a coordinate covalent bond. Brønsted–Lowry bases will therefore typically have atoms of oxygen, sulfur, nitrogen or phosphorus in their structure—these being atoms with lone pairs of electrons that can readily bind with the H^+ ion.

Remember that $H^+(aq)$ is often used interchangeably with $H_3O^+(aq)$ when discussing acids donating protons. However, from now on, we will consider the acidic species in aqueous solutions to be the hydronium ion (H_3O^+) and not the Arrhenius H^+ ion.

CONJUGATE ACID–BASE PAIRS

A solution of hydrochloric acid is produced when hydrogen chloride ionises in water:

$$HCl(g) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$$

You saw in Unit 2 that hydrochloric acid is considered a strong acid because this reaction is considered irreversible, with virtually 100% proton transfer, resulting in the complete ionisation of HCl into H_3O^+ and Cl^- ions.

In most Brønsted–Lowry acid–base reactions, the proton transfer is not 100% complete in the direction of reactants to products. Instead, a state of dynamic

equilibrium exists between the reactants and products. For example, ethanoic acid, CH_3COOH (also called acetic acid), is a weak acid that ionises in water according to the following equation:

$$CH_3COOH(l) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

The double arrow in this equation means the acid–base reaction is significant in both directions: in the forward reaction, the CH_3COOH molecule donates a proton to H_2O (which accepts it) to form the hydronium ion and the ethanoate (acetate) ion; in the reverse reaction, the H_3O^+ ion donates a proton to the CH_3COO^- ion (which accepts it) to re-form the CH_3COOH and H_2O molecules. On both sides of this equation, one substance donates a proton and another substance accepts a proton. In this case, both the forward and reverse reactions involve proton transfer, meaning that the equilibrium mixture has *two* Brønsted–Lowry acids and *two* Brønsted–Lowry bases.

You can also see this illustrated in the reaction between a base (such as ammonia, NH_3) and water:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Here, H_2O acts as the acid in the forward reaction, donating a proton to NH_3 to form the ammonium ion, NH_4^+, and the hydroxide ion, OH^-. In the reverse reaction, the NH_4^+ ion acts as the acid, donating a proton to the OH^- ion, re-forming the NH_3 and H_2O molecules.

To illustrate this even further, consider a generalised reaction between an acid (HA) and a base (B), i.e.:

$$HA(aq) + B(aq) \rightleftharpoons A^-(aq) + BH^+(aq)$$

In the forward reaction, HA donates a proton, which is accepted by B; this means that HA is a Brønsted–Lowry acid and B is a Brønsted–Lowry base. In the reverse direction, BH^+ donates a proton, which is accepted by A^-; this means that BH^+ is a Brønsted–Lowry acid and A^- is a Brønsted–Lowry base.

Acids and bases such as HA and A^- (or BH^+ and B) that differ in their chemical structure by a single proton are called acid–base conjugate pairs. Every acid has a **conjugate base**, and every base has a **conjugate acid**. A conjugate base of an acid is the acid with a single proton removed. A conjugate acid of a base is the base with a proton added.

In our generalised acid–base reaction, the acid–base conjugate pairs are as follows:

HA(aq)	+	B(aq)	⇌	A^-(aq)	+	BH^+(aq)
acid		base		base		acid

The relationship between acid–base conjugate pairs for two of the reactions shown above is represented in Figures 3.1.3 and 3.1.4. In the reaction between HCl and water, as shown in Figure 3.1.3, the conjugate acid–base pairs are HCl/Cl^- and H_2O/H_3O^+ because each acid differs from its corresponding base by one proton.

In the reaction between NH_3 and H_2O, as shown in Figure 3.1.4, the conjugate acid–base pairs are NH_4^+/NH_3 and H_2O/OH^-.

Figure 3.1.5 shows the formulas of some common acids and bases and their conjugate pairs.

When acids react with water, hydrogen (H_3O^+) ions are produced. When bases react with water, hydroxide (OH^-) ions are produced.

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

acid base acid base

FIGURE 3.1.3 Conjugate acid–base pairs are formed when an acid donates a proton to a base.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

base acid acid base

FIGURE 3.1.4 The reaction between ammonia and water, showing the conjugate acid–base pairs

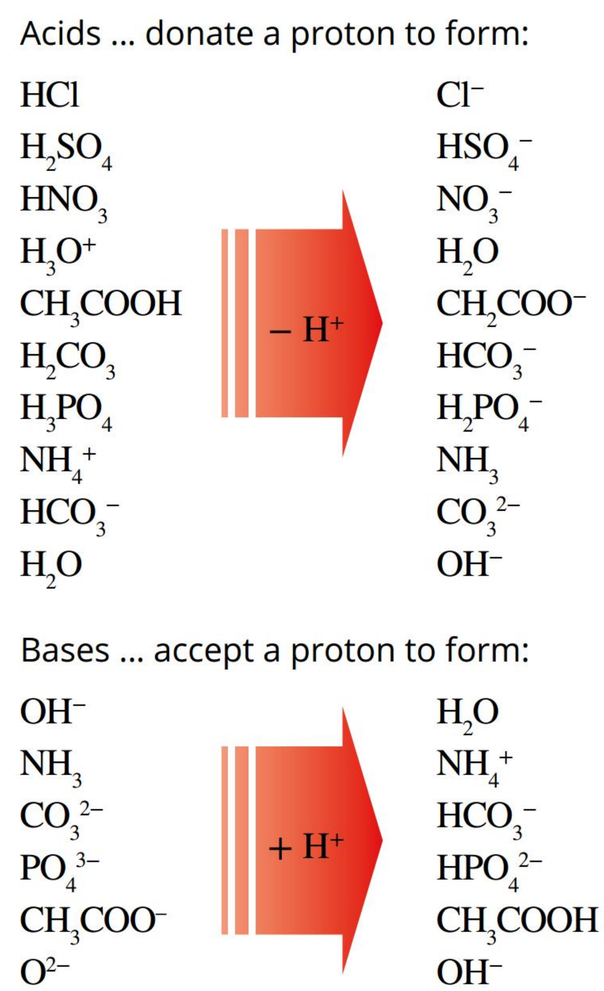


FIGURE 3.1.5 Some common acid–base conjugate pairs

AMPHIPROTIC SUBSTANCES

Some substances can donate or accept protons depending on what they are reacting with. Therefore, they can behave as either acids or bases. Such substances are said to be **amphiprotic**. You saw an example of this above with water acting as both an acid and a base depending on which substance it reacts with.

In the reaction between HCl and H_2O, water gains a proton from HCl and acts as a base:

$$HCl(g) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$$

However, in the reaction below, water donates a proton to NH_3 and acts as an acid:

$$NH_3(aq) + H_2O\ (l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

These reactions are represented in Figure 3.1.6.

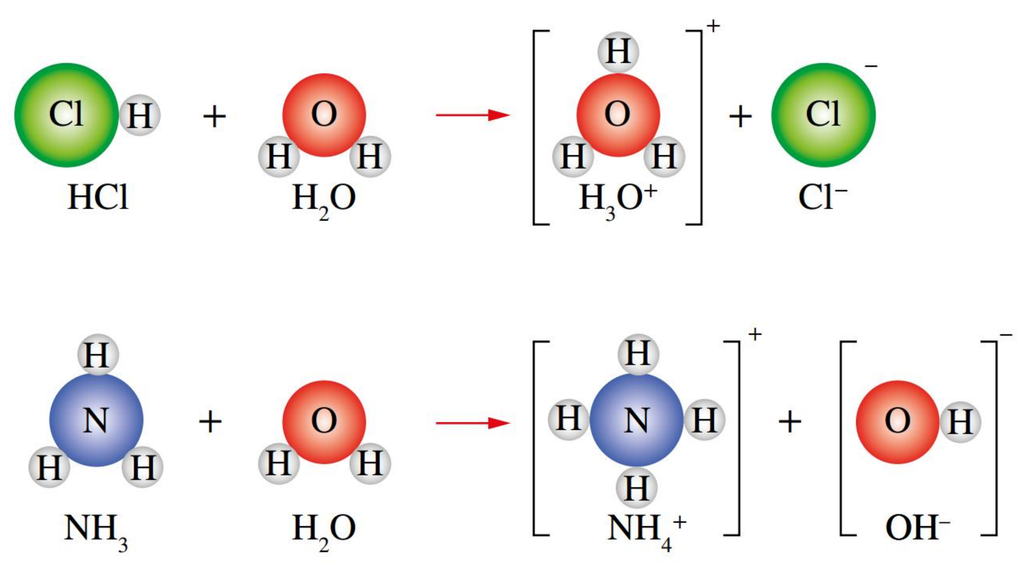


FIGURE 3.1.6 The amphiprotic nature of water is demonstrated by its reactions with HCl and NH_3.

It is evident that water can act as either an acid or a base, depending on the **solute** present.

If the solute is a stronger acid than water, then water will react as a base. If the solute is a stronger base than water, then water will react as an acid. You will consider the strengths of acids and bases (and their conjugate pairs) in the next module.

Some common amphiprotic substances are H_2O, HCO_3^-, $H_2PO_4^-$ and HSO_4^-.

When an amphiprotic substance is placed in water, it reacts as both an acid and a base. For example, the hydrogen carbonate ion (HCO_3^-) reacts according to the equations:

$$\underset{\text{base}}{HCO_3^-(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

$$\underset{\text{acid}}{HCO_3^-(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

Since HCO_3^- can act as both an acid and a base, it is amphiprotic.

Although both reactions are possible for all amphiprotic substances in water, generally one of these reactions dominates. The dominant reaction can be identified by measuring the pH (a measure of the **concentration** of hydrogen ion in solution) of the solution.

MONOPROTIC AND POLYPROTIC ACIDS

Monoprotic acids can donate only one proton to a base in acid–base reactions. These acids include hydrochloric acid (HCl), hydrofluoric acid (HF), nitric acid (HNO_3) and ethanoic acid (CH_3COOH).

Although ethanoic acid contains four hydrogen atoms, each molecule can donate only one proton to produce an ethanoate ion (CH_3COO^-) and is therefore a monoprotic acid. Only the hydrogen that is part of the highly polar O–H bond is donated. This hydrogen atom is called the **acidic proton**, as shown in Figure 3.1.7.

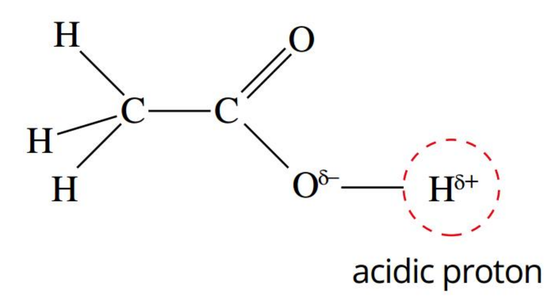


FIGURE 3.1.7 The structure of ethanoic acid. Each molecule can donate only one proton to a water molecule when ethanoic acid reacts with water.

Polyprotic acids

Some acids can donate more than one proton from each molecule and are said to be **polyprotic acids**. The number of hydrogen ions an acid can donate depends on the structure of the acid. Polyprotic acids do not donate all of their protons at once but do so in steps when reacting with a base.

Diprotic acids

Diprotic acids, such as sulfuric acid (H_2SO_4) and carbonic acid (H_2CO_3), can donate two protons.

A diprotic acid ionises in two stages; for example, sulfuric acid:

Stage 1: $H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$

Sulfuric acid is described as a **strong acid** in water because it readily donates a proton and so this stage occurs almost to completion. Virtually no H_2SO_4 molecules are found in an aqueous solution:

Stage 2: $HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$

The HSO_4^- ion formed can also act as an acid. In a $1.0\,mol\,L^{-1}$ solution, only a small proportion of those ions react further to produce H_3O^+ ions and SO_4^{2-} ions.

HSO_4^- is described as a **weak acid** because it is only partially dissociated. A double (reversible) arrow indicates that an incomplete reaction occurs. (You will learn more about strong and weak acids later in this chapter.) Therefore, a solution of sulfuric acid contains hydrogen ions, hydrogen sulfate ions and sulfate ions.

Triprotic acids

Triprotic acids can donate three protons. These include phosphoric acid (H_3PO_4) and boric acid (H_3BO_3). A triprotic acid, such as phosphoric acid, ionises in three stages:

Stage 1: $H_3PO_4(s) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$

Stage 2: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

Stage 3: $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$

Phosphoric acid is a weak acid in water. Therefore, in a $1.0\,mol\,L^{-1}$ solution of phosphoric acid, only a small proportion of the protons is donated at each **ionisation** stage. The extent of the ionisation decreases progressively from stage 1 to stage 3.

3.1 Review

SUMMARY

- The Brønsted–Lowry model describes acid–base properties in terms of proton transfer. A Brønsted–Lowry acid is a proton donor and a Brønsted–Lowry base is a proton acceptor.
- When an acid donates a proton, it forms its conjugate base. When a base accepts a proton, it forms its conjugate acid.
- Conjugate acid–base pairs are molecules or ions that differ from each other by an H^+ ion.
- A proton in solution can be represented by the hydronium ion, $H_3O^+(aq)$, or simply as the hydrogen ion, $H^+(aq)$.
- Amphiprotic substances can act as either acids or bases, depending on the substance with which they are reacting.
- A polyprotic acid can donate more than one proton to a base.
- The first ionisation of a diprotic acid occurs to a greater extent than the second ionisation. In a triprotic acid, the third ionisation occurs to the least extent.

KEY QUESTIONS

Describe

1 Identify the two acid–base conjugate pairs in the following reaction. In each case, write the acid first:

$H_2SO_4(aq) + Cl^-(aq) \rightarrow HSO_4^-(aq) + HCl(aq)$

2 Identify the conjugate of the acid or base that is written in bold for each of the following equations.

a $HF(aq) + \mathbf{OH^-}(aq) \rightarrow H_2O(l) + F^-(aq)$

b $HCOOH(aq) + \mathbf{H_2O}(l) \rightarrow H_3O^+(aq) + HCOO^-(aq)$

c $CH_3NH_2(aq) + HCl(aq) \rightarrow \mathbf{CH_3NH_3^+}(aq) + Cl^-(aq)$

3 Describe a Brønsted–Lowry acid. In your answer, refer to HCl.

4 Identify the change(s) observed in a substance as it acts as a Brønsted–Lowry base.

Apply

5 Explain why the reaction between a solution of sodium hydroxide and a solution of hydrochloric acid is a Brønsted–Lowry acid–base reaction.

6 Determine the conjugate acid of the following bases.

a NH_3

b CH_3COO^-

c HPO_4^{2-}

d CO_3^{2-}

7 Construct a structural formula of the monoprotic ethanoic acid molecule. Identify which proton is donated in an acid–base reaction. Use Figure 3.1.7 on page 61 if needed.

8 Explain why a hydrogen ion is also a proton.

Analyse

9 Distinguish between a diprotic and an amphiprotic substance. Use examples.

10 Construct an equation to show each of the following acting as an acid and a base with water.

a HCO_3^-

b HPO_4^{2-}

c HSO_4^-

d H_2O

11 Explain why HSO_4^- is an amphiprotic substance but H_2SO_4 is a diprotic acid.

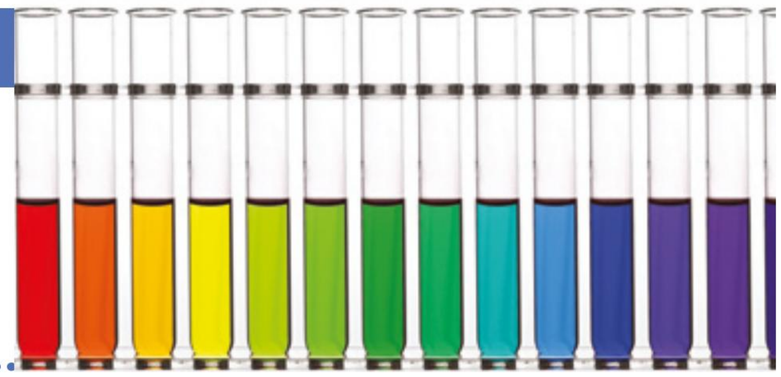
12 Distinguish between the products formed when water acts as an acid or a base.

13 Describe why the Arrhenius model is useful and explain why the Brønsted–Lowry model is better.

3.2 Strength of acids and bases

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- distinguish between strong and weak acids and bases in terms of the extent of dissociation, reaction with water and electrical conductivity
- distinguish between the terms 'strong' and 'concentrated' for acids and bases.



The acid solutions in the two beakers shown in Figure 3.2.1 are of equal concentration, yet the acid in the beaker on the left reacts more vigorously with zinc than the acid on the right. The acid on the left is described as a stronger acid than the one in the beaker on the right.

In Module 3.1, you learnt that the Brønsted–Lowry model defines acids as proton donors and bases as proton acceptors. In this module, you will investigate the differences between:

- strong and weak acids
- strong and weak bases.

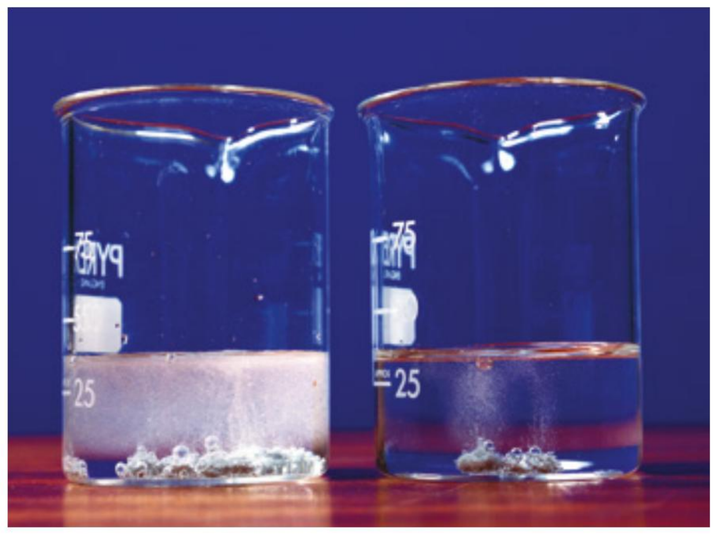


FIGURE 3.2.1 Zinc reacts more vigorously with a strong acid (left) than with a weak acid (right). The acid solutions are of equal concentration and volume.

ACID AND BASE STRENGTH

Experiments show that different acid solutions of the same concentration do not have the same pH (a measure of the amount of hydrogen ion in solution—pH will be looked at more closely in the following module).

Some acids can donate a proton more readily than others. The Brønsted–Lowry model describes the strength of an acid as its ability to donate protons (i.e. hydrogen ions) to a base. The strength of a base is a measure of its ability to accept protons from an acid.

Since aqueous solutions of acids and bases are most commonly used, it is convenient to use an acid's tendency to donate a proton to water, or a base's tendency to accept a proton from water, as a measure of its strength.

Strong acids

As you saw previously, when hydrogen chloride gas (HCl) is bubbled through water, it ionises completely—virtually no HCl molecules remain in the solution, as shown in Figure 3.2.2a. Similarly, pure HNO_3 and H_2SO_4 are covalent molecular compounds, which also ionise completely in water:

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
$$HNO_3(l) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$
$$H_2SO_4(l) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$$

The single arrow → in each equation above indicates that the ionisation reaction is complete.

Acids that readily donate a proton are called strong acids. Strong acids donate protons easily. Therefore, solutions of strong acids contain ions, with virtually no unreacted acid molecules remaining.

A general equation for the ionisation of a strong acid in water can be written as

$$HA(aq) + H_2O(l) \rightarrow A^-(aq) + H_3O^+(aq)$$

For the purposes of your studies, there are only seven acids that are considered strong acids—all of which are listed in Table 3.2.1. All are monoprotic acids except for sulfuric acid, which is diprotic. Hydrochloric acid, sulfuric acid and nitric acid are the most common strong acids.

TABLE 3.2.1 The seven strong acids, including chemical formulas, the ions they produce and common applications

Acid name	Formula	Ions	Notes/Applications
*hydrochloric acid	HCl	H_3O^+ / Cl^-	used in cleaning (e.g. removing rust), pH regulation (e.g. swimming pools)
hydrobromic acid	HBr	H_3O^+ / Br^-	used in organic synthesis, particularly for producing organo-bromides
hydroiodic acid	HI	H_3O^+ / I^-	used as a reducing agent and in the synthesis of iodine-containing organic compounds
*nitric acid	HNO_3	H_3O^+ / NO_3^-	strong oxidising acid that is used to dissolve noble metals such as gold, platinum and palladium; also, used in fertiliser production (e.g. ammonium nitrate), explosives and metal etching
chloric acid	$HClO_3$	H_3O^+ / ClO_3^-	strong oxidising agent that is used in a range of industrial processes
perchloric acid	$HClO_4$	H_3O^+ / ClO_4^-	strong oxidising agent that is used for preparing perchlorate salts in explosives, rocket propellants and batteries
*sulfuric acid	H_2SO_4	H_3O^+ / HSO_4^- H_3O^+ / SO_4^{2-}	used in car batteries (lead–acid batteries), fertiliser production and as an industrial catalyst

* Indicates strong acids that you are expected to know as part of this course.

Weak acids

Vinegar is a solution of ethanoic acid. Pure ethanoic acid is a polar covalent molecular compound that ionises in water to produce hydrogen ions and ethanoate ions. In a 1.0 mol L^{-1} solution of ethanoic acid (CH_3COOH), only a small proportion of ethanoic acid molecules are dissociated at any one time (Figure 3.2.2b). A 1.0 mol L^{-1} solution of ethanoic acid contains a high proportion of CH_3COOH molecules and only some hydrogen ions and ethanoate ions. At 25°C, in a 1.0 mol L^{-1} solution of ethanoic acid, the concentrations of $CH_3COO^-(aq)$ and H_3O^+ are only about 0.004 mol L^{-1}.

The partial ionisation of a weak acid is shown in an equation using reversible (double) arrows:

$$\underset{\text{acid}}{CH_3COOH(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons CH_3COO^-(aq) + H_3O^-(aq)$$

Therefore, ethanoic acid is described as a weak acid in water. This can be seen in Figure 3.2.2 on page 66.

The generalised equation for the ionisation of a weak acid in water can be written as:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

You will note this equation takes the same form as the generalised equation for the ionisation of a strong acid, except for the presence of the double arrows. This is indicative of a reaction that is appreciable in both directions (i.e. reversible) and that a dynamic equilibrium will be readily established in a closed system.

Organic acids/carboxylic acids

Ethanoic acid is one example of a broad class of weak acids known as organic acids. Organic acids contain carbon atoms and one or more functional groups such as carboxyl (–COOH), sulfonic (–SO_3H) or phosphoric (–PO_3H_2) groups. Organic acids generally contain acidic H atoms (that are donated to bases in acid–base reactions) and non-acidic H atoms (that remain bonded to carbon or other atoms and do not participate in acid–base reactions).

The most common group of organic acids is the carboxylic acids, which contain one or more carboxyl groups (–COOH). Table 3.2.2 lists some common carboxylic

acids. The first four carboxylic acids listed are monoprotic acids that form part of a homologous series containing 1, 2, 3 and 4 carbon atoms, respectively. The fifth example, oxalic acid, is a dicarboxylic acid, containing two carboxyl groups – it has the capacity to donate two protons to a base and is therefore a diprotic acid. Citric acid is a tricarboxylic acid, containing three carboxyl group, making it a weak triprotic acid.

You will encounter organic acids, carboxylic acids and homologous series in more detail when you study organic chemistry in Unit 4.

TABLE 3.2.2 Common carboxylic acids including chemical formulas, the ions they produce and common applications

Acid name (common name)	Formula (condensed structural formula)	Ions	Notes/Applications
methanoic acid (formic acid)	CH_2O_2 (HCOOH)	H_3O^+ / $HCOO^-$	the simplest carboxylic acid, present in ant venom
ethanoic acid (acetic acid)	$C_2H_4O_2$ (CH_3COOH)	H_3O^+ / CH_3COO^-	the main component of vinegar
propanoic acid (propionic acid)	$C_3H_6O_2$ (C_2H_5COOH)	H_3O^+ / $C_2H_5COO^-$	used as a preservative in food products
butanoic acid (butyric acid)	$C_4H_8O_2$ (C_3H_7COOH)	H_3O^+ / $C_3H_7COO^-$	present in butter and contributes to its characteristic smell
oxalic acid*	$C_2H_2O_4$ (HOOC–COOH)	H_3O^+ / $HC_2O_4^-$ H_3O^+ / $C_2O_4^{2-}$	a dicarboxylic acid in plants such as spinach and rhubarb
citric acid*	$C_6H_8O_7$ (HOC(COOH) $(CH_2COOH)_2$)	H_3O^+ / $H_2C_6H_5O_7^-$ H_3O^+ / $HC_6H_5O_7^{2-}$ H_3O^+ / $C_6H_5O_7^{3-}$	the acidic, sour-tasting, component of citrus fruits such as lemons and oranges

* Oxalic acid is the common name for ethanedioic acid; citric acid is the common name for 2-hydroxy-1,2,3-propane-tricarboxylic acid.

Inorganic acids/carbonic acids

Examples of inorganic weak acids are nitrous acid, HNO_2, hydrofluoric acid, HF, and carbonic acid, H_2CO_3. Carbonic acid is particularly important in environmental chemistry, and plays a crucial role in the carbon cycle and the regulation of pH in natural waters. It is formed when carbon dioxide, CO_2, dissolves in water such as in oceans, lakes and rain:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Its significance lies in the equilibria reactions set up between CO_2, H_2CO_3 and HCO_3^- (hydrogen carbonate). When dissolved in water, H_2CO_3 produces HCO_3^- ions and hydronium ions (H_3O^+), ultimately leading to increased acidification of natural waters:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

The HCO_3^- ion undergoes further reaction with water to produce the carbonate ion (CO_3^{2-}):

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

The balance between carbonic acid, hydrogen carbonate and carbonate ions helps maintain (or buffer) the pH of natural waters in a range suitable for aquatic life. You will learn more about buffers in Module 3.5.

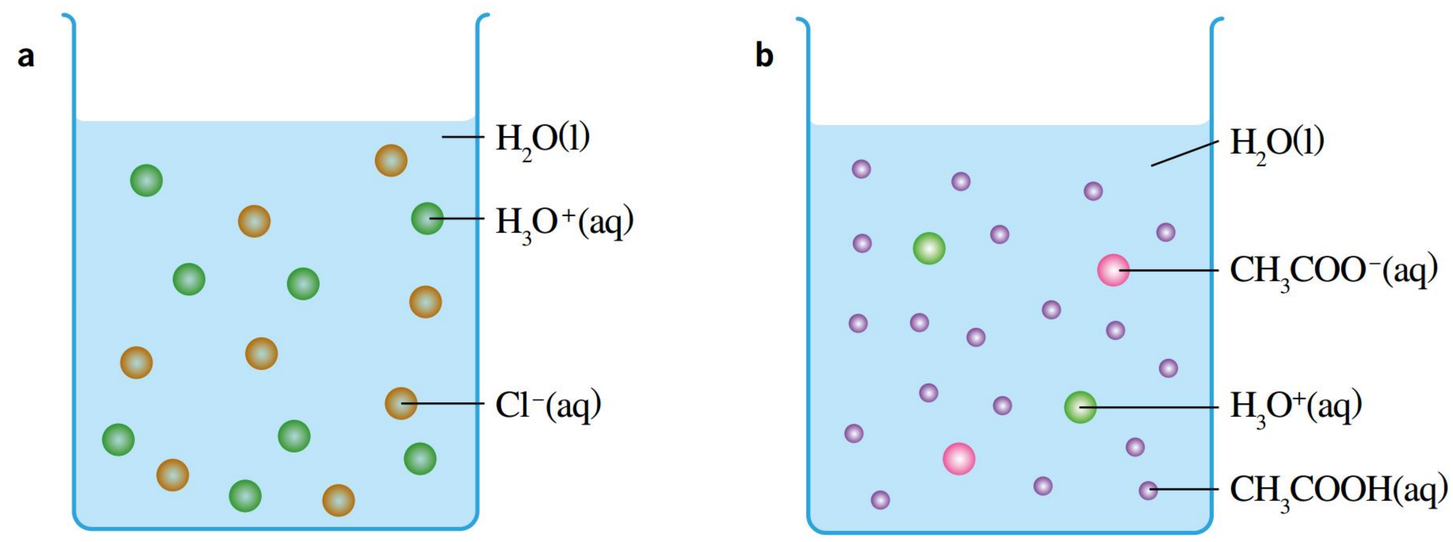


FIGURE 3.2.2 (a) In a 1.0 mol L^{-1} solution of hydrochloric acid, the acid molecules are completely dissociated in water. (b) In a 1.0 mol L^{-1} solution of ethanoic acid, only a small proportion of the ethanoic acid molecules are dissociated.

Differences in conductivity

Acids of equal concentrations can have different abilities to conduct an electric current. When copper electrodes are immersed in a 1.0 mol L^{-1} solution of hydrochloric acid and connected to an electric circuit containing a light globe, the globe glows brightly. When the hydrochloric acid is substituted with a 1.0 mol L^{-1} solution of ethanoic acid, the globe only glows faintly. This provides further evidence that hydrochloric acid is a stronger acid than ethanoic acid. The brighter light indicates a greater number of ions present in a solution of hydrochloric acid than in ethanoic acid (as shown in Figure 3.2.2).

Strong bases

The ionic compound sodium oxide (Na_2O) dissociates in water, releasing sodium ions (Na^+) and oxide ions (O^{2-}). The oxide ions react completely with the water, accepting a proton to form hydroxide ions (OH^-):

$$Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$$

Sodium oxide is an example of a **strong base**. Strong bases accept protons easily.

Other examples of strong bases are hydroxide salts that readily dissolve (**dissociate**) in water to release hydroxide ions, including the group 1 metal hydroxides and the heavier group 2 metal hydroxides listed in Table 3.2.3. These salts are very soluble in water and, up to the point of solution saturation, completely dissociate into their soluble ions. For example:

$$NaOH(aq) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

TABLE 3.2.3 Common bases, including chemical formulas, the ions they produce and common applications

Name	Formula	Ions	Notes/Applications
*lithium hydroxide	LiOH	Li^+ / OH^-	used in batteries (especially lithium-ion batteries), carbon dioxide removal systems and lubricants
*sodium hydroxide	NaOH	Na^+ / OH^-	commonly used in soap making, chemical manufacturing (e.g. production of chlorine), cleaning products and water treatment
*potassium hydroxide	KOH	K^+ / OH^-	used in soap making, as a strong base in chemical reactions, in fertilisers and in the production of biodiesel
*rubidium hydroxide	RbOH	Rb^+ / OH^-	used in specialised chemical reactions and research, such as in the synthesis of other rubidium compounds, and as a strong base in certain laboratory processes

Name	Formula	Ions	Notes/Applications
calcium hydroxide	$Ca(OH)_2$	Ca^{2+} / $2OH^-$	used in construction (e.g. as slaked lime in mortar), water treatment and to adjust soil pH in agriculture
strontium hydroxide	$Sr(OH)_2$	Sr^{2+} / $2OH^-$	used in the production of strontium compounds for fireworks
*barium hydroxide	$Ba(OH)_2$	Ba^{2+} / $2OH^-$	used in the refining of lubricants and the treatment of certain oils and fats

* Indicates strong bases that you are expected to know as part of this course.

Weak bases

Ammonia is a covalent molecular compound that ionises in water by accepting a proton. This ionisation process can be represented by the equation:

$$\underset{\text{base}}{NH_3(g)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

This reaction proceeds because the ammonia molecule contains a non-bonding pair of electrons on the nitrogen atom that can bind to a proton (H^+ ion). Ammonia behaves as a base because it gains a proton. Water has donated a proton and so it behaves as an acid.

Only a small proportion of ammonia molecules are ionised at any instant, so a $1.0\,mol\,L^{-1}$ solution of ammonia contains mostly ammonia molecules together with a smaller number of ammonium ions and hydroxide ions. This is shown by the double arrow in the equation. Ammonia is a **weak base** in water.

The generalised equation for the ionisation of a weak base in water can be written as:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

Being able to write generalised equations such as this, for weak acid and weak base equilibria, will assist you greatly in understanding ideas in the following modules of this chapter.

Examples of weak bases (other than ammonia) include a class of compounds known as amines. Amines are organic compounds that contain a nitrogen atom bonded to one or more alkyl groups. Figure 3.2.3 shows the structure of the simplest amine, methylamine (CH_3NH_2), which shows a central nitrogen atom bonded to a methyl ($-CH_3$) group and two hydrogen atoms.

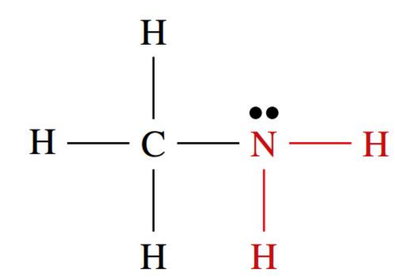


FIGURE 3.2.3 Primary amines contain the amino functional group, $-NH_2$ (in red). There are two non-bonding electrons on the nitrogen atom.

Amines are weak bases because (like ammonia) they possess a pair of non-bonding electrons on the nitrogen atom, allowing them to accept protons via a coordinate covalent bond.

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Relative strength of acids and bases—stoichiometry

In Unit 2, and again above, you saw that the relative strengths of acids and bases is determined by the extent of **dissociation** and/or ionisation. Strong acids and bases ionise or dissociate completely when dissolved in (react with) water. Conversely, weak acids and bases only ionise to a limited extent.

The Brønsted–Lowry model allows you to interpret acid/base strength in terms of how readily protons are donated or accepted. Strong acids readily donate (close to) 100% of protons to water molecules, while weak acids only donate a small fraction of their protons. The strength of bases depends on their ability to accept protons, and strong bases accept protons more readily than weak bases.

An alternative way of defining strong and weak acids can be drawn from stoichiometry. Strong acids react with water in such a way that they completely (100%) ionise to produce $H_3O^+(aq)$. Because this reaction goes to completion, the amount of H_3O^+ generated can be calculated directly from the stoichiometry of the balanced chemical equation. We can represent this using a generalised form of a monoprotic acid, HA:

$$HA(aq) + H_2O(l) \rightarrow A^-(aq) + H_3O^+(aq)$$

By contrast, weak acids establish a dynamic equilibrium and only partially ionise in water:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

As a result, the amount of H_3O^+ produced by a weak acid is less than what is predicted by the stoichiometry of the balanced equation.

We can define strong and weak acids as follows:

- strong acids fully react with water to produce stoichiometric amounts of H_3O^+
- weak acids partially react with water, producing less than stoichiometric amounts of H_3O^+.

Similarly, the definitions for bases are as follows.

- strong bases fully react with water to produce stoichiometric amounts of OH^-
- weak bases partially react with water, producing less than stoichiometric amounts of OH^-.

For weak acids and bases, the quantities of H_3O^+ or OH^- formed depend on the equilibrium constant for the specific reaction, and you will need to use ICE table calculations like those in the previous chapter to determine equilibrium concentrations. Weak acid and weak base equilibria are explored further in module 3.5.

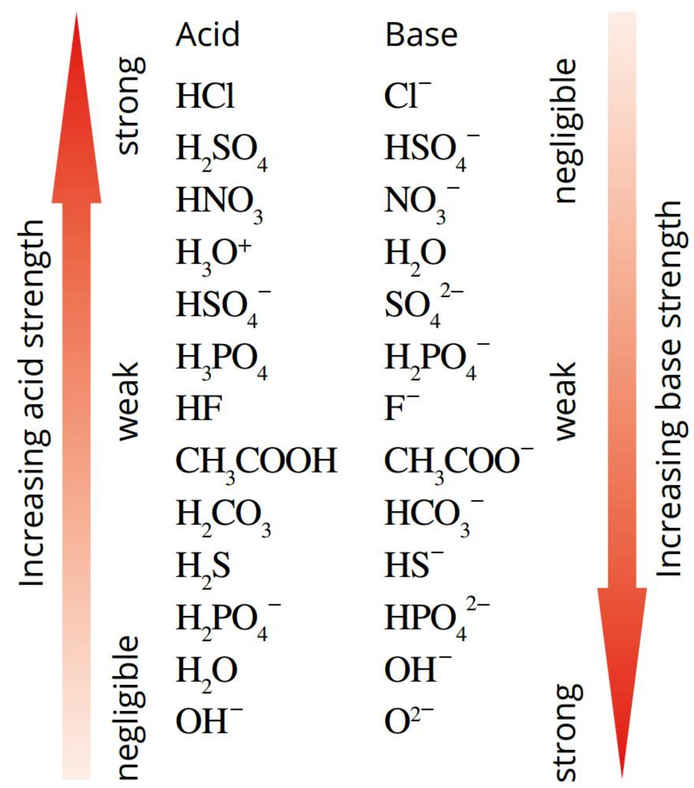


FIGURE 3.2.4 The relative strengths of some conjugate acid–base pairs

Relative strength of conjugate acid–base pairs

You will recall from Module 3.1 that conjugate acids and bases differ by one proton (H^+). In the reaction represented by the equation:

$$HF(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + F^-(aq)$$

HF is the conjugate acid of F^- and OH^- is the conjugate base of H_2O. HF and F^- are a conjugate acid–base pair. H_2O and OH^- are another conjugate acid–base pair in this reaction.

The stronger an acid is, the weaker its conjugate base is. Similarly, the stronger a base is, the weaker its conjugate acid is. The relative strengths of some conjugate acid–base pairs is shown in Figure 3.2.4.

Strength vs concentration

When referring to solutions of acids and bases, it is important not to confuse the terms 'strong' and 'weak' with 'concentrated' and 'dilute'. Concentrated and dilute describe the amount of acid or base dissolved in a given volume of solution. Hydrochloric acid is a strong acid because it readily donates protons. A **concentrated solution** of hydrochloric acid can be prepared by bubbling a large amount of hydrogen chloride into a given volume of water. By using only a small amount of hydrogen chloride, a dilute solution of hydrochloric acid would be produced.

However, in both cases, the hydrogen chloride is completely ionised—it is a strong acid. Similarly, a solution of ethanoic acid may be concentrated or dilute. However, because it is partially dissociated, it is a weak acid (Figure 3.2.5).

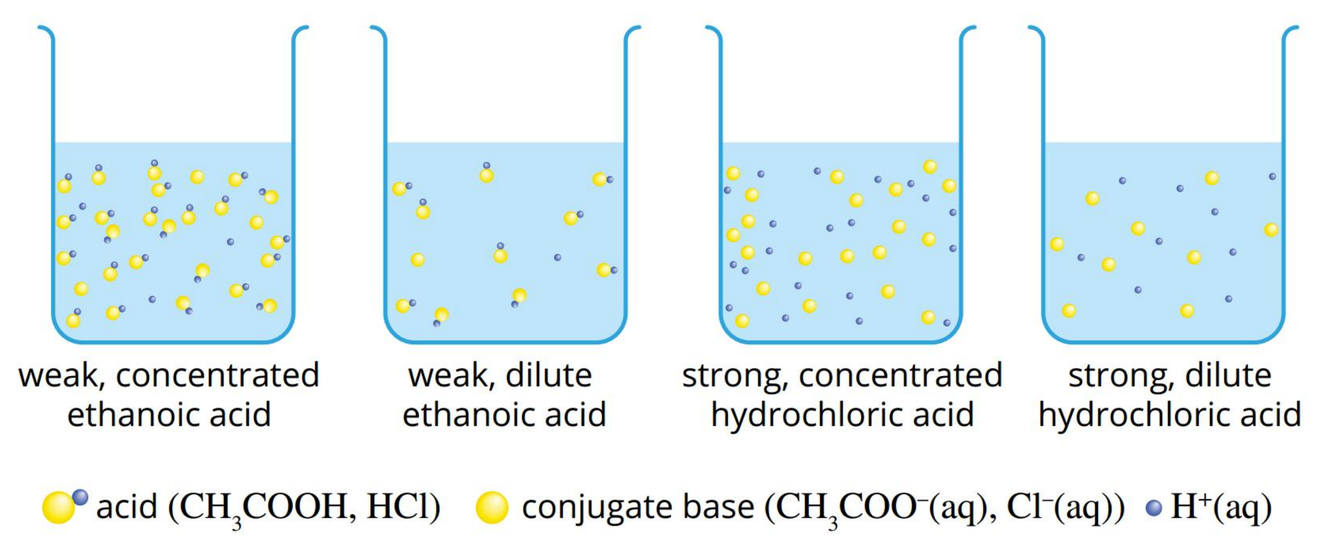


FIGURE 3.2.5 The concentration of ions in an acid solution depends on both the concentration and strength of the acid.

Terms describing acids as 'weak' or 'strong', or solutions as 'dilute' or 'concentrated', are qualitative (or descriptive) terms. Solutions can be given accurate, quantitative descriptions by stating concentrations in mol L^{-1} (M) or g L^{-1}.

3.2 Review

SUMMARY

- In the context of acids and bases, the terms 'strong' and 'weak' refer to the relative tendency to accept or donate protons.
  - A strong acid donates a proton more readily than a weak acid.
  - A strong base accepts a proton more readily than a weak base.
- From a stoichiometric point of view:
  - strong acids fully react with water to produce stoichiometric amounts of H_3O^+
  - weak acids partially react with water to produce less than stoichiometric amounts of H_3O^+
  - strong bases fully react with water to produce stoichiometric amounts of OH^-
  - weak bases partially react with water to produce less than stoichiometric amounts of OH^-
- The stronger an acid, the weaker its conjugate base. The stronger a base, the weaker its conjugate acid.
- A concentrated acid or base contains more moles of solute per litre than a dilute acid or base.

KEY QUESTIONS

Describe

1 Identify key strong acids and strong bases (as described in the Senior Chemistry syllabus).

2 Identify key weak acids and weak bases (as described in the Senior Chemistry syllabus).

3 Use balanced equations to show that in water:

a $HClO_4$ is a strong acid

b HCN is a weak acid

c CH_3NH_2 is a weak base.

Apply

4 Identify which of the following is a reaction of a strong acid and which is a reaction of a weak acid. Explain how you came to form this conclusion.

A $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

B $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

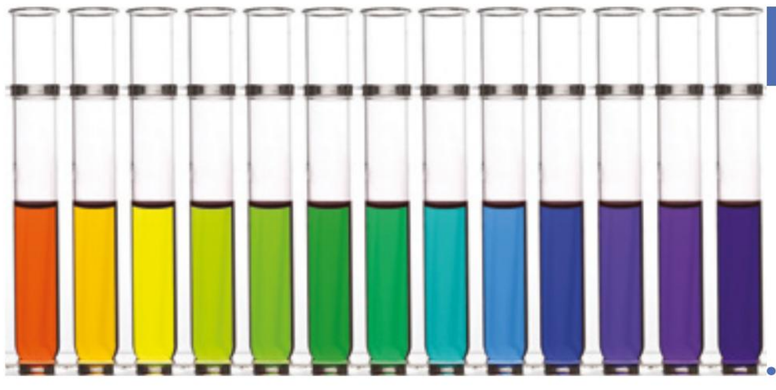
5 Construct balanced equations for the three ionisation stages of arsenic acid (H_3AsO_4).

Analyse

6 Perchloric acid is a stronger acid than ethanoic acid. Explain which 1.0 mol L^{-1} solution of each acid would be a better conductor of electricity.

7 Given that the first ionisation process for a polyprotic acid occurs to a greater extent than the second or third ionisation processes. Determine whether you would expect $H_2PO_4^-$ or HPO_4^{2-} to be a stronger acid.

3.3 Acidity of solutions



BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand the pH scale, which is a measure of acidity
- understand the pOH scale, which is a measure of basicity
- understand the relationship between the concentration of hydrogen and hydroxide ions in different solutions.

IONIC PRODUCT OF WATER

You will recall from Unit 2 that water molecules can react with each other as represented by the equation:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The production of the H_3O^+ ion and OH^- ion within this reaction can be seen in Figure 3.3.1.

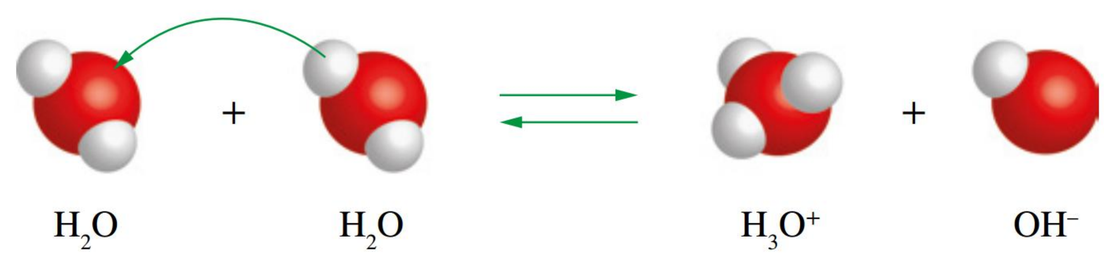


FIGURE 3.3.1 The self-ionisation of water molecules

Pure water undergoes this **self-ionisation** to a very small extent. In this reaction, water behaves as both a very weak acid and as a very weak base, producing one hydrogen ion (H_3O^+) for every one hydroxide ion (OH^-). Water is displaying amphiprotic properties.

The extent of **ionisation** for this process can be determined by considering the equilibrium constant, remembering that pure liquids and/or solvents are omitted from the equilibrium expression:

$$K_w = [H_3O^+][OH^-]$$

The important significance of this particular equilibrium expression in chemistry means that the equilibrium constant is given its own special symbol, K_w, and is called the **ionic product of water** (or **ionisation constant of water**).

The concentration of hydrogen and hydroxide ions is very low. In pure water at 25°C, the H_3O^+ and OH^- concentrations are each 1.00×10^{-7} mol L^{-1}. This gives a value of the ionic product of water, K_w, as:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 25°C$$

The equilibrium process lies so far to the left that for each H_3O^+ ion present in a glass of water, there are 560 million H_2O molecules!

Experimental evidence shows that all aqueous solutions contain both H_3O^+ and OH^- ions, and that the product of their molar concentrations, $[H_3O^+][OH^-]$, is always 1.00×10^{-14} at 25°C. This means that if either $[H_3O^+]$ or $[OH^-]$ increases, then the concentration of the other must decrease proportionally.

A final point worth noting about the K_w expression is that you may also see it written as:

$$K_w = [H^+][OH^-]$$

You saw earlier, in Module 3.1, how the acidic form of water can sometimes be represented as either an H^+ ion or as the hydronium ion, H_3O^+. This is because when an acid donates a proton (i.e. an H^+ ion) in solution, it is immediately accepted by a water molecule to produce the H_3O^+ ion. This version of the K_w expression is valid when the self-ionisation of water is represented as:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Square brackets [ ] are often used to represent molar concentration.

Acidic and basic solutions

In solutions of acidic substances, H_3O^+ ions are formed by the reaction of the acid with water, as well as from the self-ionisation of water. So, the concentration of H_3O^+ ions will be greater than $10^{-7}\,mol\,L^{-1}$ at 25°C. Since the product $[H_3O^+][OH^-]$ remains constant, the concentration of OH^- ions in an **acidic solution** at this temperature must be less than $10^{-7}\,mol\,L^{-1}$.

The opposite is true for **basic solutions**. The concentration of the OH^- ions in a basic solution is greater than $10^{-7}\,mol\,L^{-1}$, and that of H_3O^+ ions is less than $10^{-7}\,mol\,L^{-1}$.

In summary, at 25°C:

- pure water and **neutral solutions**: $[H_3O^+] = [OH^-] = 10^{-7}\,mol\,L^{-1}$
- acidic solutions: $[H_3O^+] > 10^{-7}\,mol\,L^{-1}$ and $[OH^-] < 10^{-7}\,mol\,L^{-1}$
- basic solutions: $[H_3O^+] < 10^{-7}\,mol\,L^{-1}$ and $[OH^-] > 10^{-7}\,mol\,L^{-1}$.

The higher the concentration of H_3O^+ ions in a solution, the more acidic the solution is.

Calculating the concentration of H_3O^+ in aqueous solutions

The expression for K_w can be used to determine the concentrations of hydrogen and hydroxide ions in solution, knowing that the value of K_w in solutions at 25°C is 1.00×10^{-14}.

Worked example 3.3.1

CALCULATING THE CONCENTRATION OF HYDROGEN AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

Calculate the concentration of:

- H_3O^+ ions
- OH^- ions

in a $0.10\,mol\,L^{-1}$ solution of HCl at 25°C.

Thinking	Working
Determine the concentration of the hydrogen (H_3O^+) ions.	HCl is a strong acid, so it will ionise completely in solution. Each molecule of HCl donates one proton to water to form one H_3O^+ ion: $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$ Because HCl is completely ionised in water, $0.10\,mol\,L^{-1}$ of HCl will have a stoichiometrically equivalent concentration of H_3O^+ ions of $0.10\,mol\,L^{-1}$: i.e. $[H_3O^+] = 0.10\,mol\,L^{-1}$
Use the expression for the ionisation constant of water to calculate the concentration of OH^- ions.	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[OH^-] = \frac{1.00 \times 10^{-14}}{[H_3O^+]}$ Since $[H_3O^+] = 0.10\,mol\,L^{-1}$ $[OH^-] = \frac{1.00 \times 10^{-14}}{0.10}$ $= 1.0 \times 10^{-13}\,mol\,L^{-1}$

➤ Try yourself 3.3.1

CALCULATING THE CONCENTRATION OF HYDROGEN AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

Calculate the concentration of:

- H_3O^+ ions
- OH^- ions

in a 5.6×10^{-6} mol L^{-1} solution of HNO_3 at 25°C.

THE pH SCALE AND THE pOH SCALE

Introducing the p-function

The study of chemistry often requires quantifying extremely large or small values, spanning a vast range of numerical magnitudes. For instance, the concentration of H_3O^+ ions in aqueous solutions can range from as low as 10^{-15} mol L^{-1} in highly diluted solutions to as high as 10 mol L^{-1} in very concentrated solutions—a difference spanning 16 orders of magnitude. To simplify the handling and comparison of such wide-ranging values, chemists use the p-function.

The p-function transforms large quantities into manageable logarithmic values, offering a concise and intuitive way to represent and interpret extreme numerical ranges. It is defined as the negative base-10 logarithm of a given quantity, and is expressed as:

$$pX = -\log_{10}(X)$$

where X represents the quantity of interest. By applying the p-function, complex numerical values, such as concentrations or equilibrium constants, are converted into more concise and manageable forms. This transformation aids in simplifying calculations and allows for easier comparison and interpretation of chemical properties across different systems.

One example where the p-function is commonly used is in its application to K_w, the ionic product of water. You saw above that:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 25°C$$

Applying the p-function to the numerical value of K_w, gives you:

$$-\log K_w = -\log ([H_3O^+][OH^-])$$

which rearranges to:

$$pK_w = -\log[H_3O^+] + (-\log[OH^-]) = -\log_{10}(1.00 \times 10^{-14})$$

The numerical value of the right-hand side of this equation is 14; therefore:

$$pK_w = 14 \text{ at } 25°C$$

While this value for pK_w may seem unremarkable to you at this stage, you will see in the following sections how useful this quantity can be.

In addition, the terms '$-\log[H_3O^+]$' and '$-\log[OH^-]$' represent two important quantities in chemistry, namely pH (which you first met in Unit 2) and pOH. Both quantities are discussed in detail below.

Definition of pH

As noted above, the range of H_3O^+ concentrations in solutions is so great that a convenient scale, called the **pH scale**, has been developed to measure **acidity**. The pH scale was first proposed by the Danish scientist Sören Sörenson in 1909 as a way of expressing levels of acidity in terms of the concentration of hydronium (H_3O^+) ions. The pH of a solution can be expressed as:

$$pH = -\log_{10}[H_3O^+]$$

Alternatively, this expression can be rearranged to give:

$$[H_3O^+] = 10^{-pH} \text{ mol } L^{-1}$$

The pH scale eliminates the need to write cumbersome powers of 10 when we describe hydronium ion concentration. The use of pH greatly simplifies the

measurement and calculation of acidity. Since the scale is based upon the negative logarithm of the hydrogen ion concentration, the pH of a solution *decreases* as the concentration of hydrogen ions *increases*.

For reasons outlined above, regarding the interchangeability of the H^+ ion and the H_3O^+ ion, you may also see the pH expression written as:

$$pH = -\log_{10}[H^+]$$

Whether you express acidity in terms of $[H^+]$ or $[H_3O^+]$, the magnitude and units of concentration are identical, and so the calculated pH value will also be identical.

pH of acidic and basic solutions

Figure 3.3.2 shows a pH meter, which is used to accurately measure the pH of a solution.

FIGURE 3.3.2 A pH meter is used to measure the acidity of a solution.

Acidic, basic and neutral solutions can be defined in terms of their pH at 25°C.

- Neutral solutions have a pH equal to 7.0.
- Acidic solutions have a pH less than 7.0.
- Basic solutions have a pH greater than 7.0.

On the pH scale, the most acidic solutions have pH values slightly less than 0.0 and the most basic solutions have values of about 14.0. The pH values of some common substances are provided in Table 3.3.1.

TABLE 3.3.1 pH values of some common substances at 25°C

Solution	pH	$[H_3O^+]$ (M)	$[OH^-]$ (M)	$[H_3O^+] \times [OH^-]$
1.0 mol L^{-1} HCl	0.0	1	10^{-14}	10^{-14}
lemon juice	3.0	10^{-3}	10^{-11}	10^{-14}
vinegar	4.0	10^{-4}	10^{-10}	10^{-14}
tomatoes	5.0	10^{-5}	10^{-9}	10^{-14}
rainwater	6.0	10^{-6}	10^{-8}	10^{-14}
pure water	7.0	10^{-7}	10^{-7}	10^{-14}
seawater	8.0	10^{-8}	10^{-6}	10^{-14}
soap	9.0	10^{-9}	10^{-5}	10^{-14}
oven cleaner	13.0	10^{-13}	10^{-1}	10^{-14}
1.0 mol L^{-1} NaOH	14.0	10^{-14}	10^{-0}	10^{-14}

The reactions of acids and bases are important in a large variety of everyday applications. The high acidity of gastric juices is essential for protein digestion in the stomach. There is a complex system of pH control in your blood because even small deviations from the normal pH range of 7.35–7.45 for any length of time can lead to serious illness and death.

A solution with pH 2.0 has 10 times the concentration of hydrogen ions as one of pH 3.0. The solution of pH 2.0 has one-tenth the concentration of hydroxide ions as one of pH 3.0.

Definition of pOH

While pH is a measure of the acidity of an aqueous solution, pOH can be used as a measure of the **basicity** of a solution, i.e. a measure of how basic a solution is in terms of the concentration of OH^- ions. The pOH of a solution can be expressed as:

$$pOH = -\log_{10}[OH^-]$$

and can be rearranged to give:

$$[OH^-] = 10^{-pOH}\ \text{mol L}^{-1}$$

Like the pH scale, the **pOH scale** extends over many orders of magnitude and eliminates the need to write cumbersome powers of 10 when we describe hydroxide ion concentration. By convention, however, the acidity (or basicity) of a solution is commonly represented by the pH scale, and the use of pOH is typically restricted to situations that specifically focus on hydroxide ion concentration.

The relationship between pH and pOH

There is a very useful relation that can be mathematically derived from the K_w expression:

$$K_w = [H_3O^+][OH^-] \text{ at } 25°C$$

We saw above that applying the p-function to both sides of this equation gives you:

$$pK_w = -\log[H_3O^+] + (-\log[OH^-])$$

Recognising that $pK_w = 14$, and further recognising that the terms on the right-hand side of this equation are expressions for pH and pOH, you get the following very useful relationship:

$$pH + pOH = 14 \text{ at } 25°C$$

In other words, if we know either the pH or pOH of a solution, we can easily calculate the other term from this equation.

Calculations involving pH and pOH

pH can be calculated using the formula $pH = -\log_{10}[H_3O^+]$ and pOH can be calculated using $pOH = -\log_{10}[OH^-]$. Your scientific calculator has a logarithm function that will simplify pH and pOH calculations.

Worked example 3.3.2

CALCULATING THE pH OF AN AQUEOUS SOLUTION FROM $[H_3O^+]$

Calculate the pH of a solution in which the concentration of $[H_3O^+]$ is $0.14\,mol\,L^{-1}$. Express your answer to two decimal places.	
Thinking	**Working**
Identify the concentration of H_3O^+ ions in the solution.	$[H_3O^+] = 0.14\,mol\,L^{-1}$
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(0.14)$ $= 0.85$

➤ Try yourself 3.3.2

CALCULATING THE pH OF AN AQUEOUS SOLUTION FROM $[H_3O^+]$

Calculate the pH of a solution in which the concentration of $[H_3O^+]$ is $6 \times 10^{-9}\,mol\,L^{-1}$. Express your answer to two decimal places.

Worked example 3.3.3

CALCULATING pH IN A SOLUTION OF A STRONG BASE

Calculate the pH of a $0.005\,mol\,L^{-1}$ solution of $Ba(OH)_2$ at 25°C.	
Thinking	**Working**
Identify the reaction in which $Ba(OH)_2$ dissociates.	$Ba(OH)_2$ is a strong base and will completely dissociate when dissolved in water (see Table 3.2.3 on page 66). In water, each mole of $Ba(OH)_2$ completely dissociates to release 2 moles of OH^- ions: $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$

Determine the concentration of OH^- ions.	$[OH^-] = 2 \times [Ba(OH)_2]$ $= 2 \times 0.005\,mol\,L^{-1}$ $= 0.010\,mol\,L^{-1}$
Determine the concentration of H_3O^+ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-]$ $= 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.010}$ $= 1 \times 10^{-12}\,mol\,L^{-1}$
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(1 \times 10^{-12})$ $= 12.0$

➤ Try yourself 3.3.3

CALCULATING pH IN A SOLUTION OF A STRONG BASE

Calculate the pH of a $0.01\,mol\,L^{-1}$ solution of $Ba(OH)_2$ at 25°C.

Worked example 3.3.4

CALCULATING pH IN A SOLUTION WHERE THE SOLUTE CONCENTRATION IS NOT GIVEN

Calculate the pH of a solution at 25°C that contains 1.0 g sodium hydroxide (NaOH) in 100 mL of solution.

Thinking	Working
Determine the number of moles of NaOH.	$n(NaOH) = \frac{m}{M}$ $n(NaOH) = \frac{1.0}{40.00}$ $= 0.025\,mol$
Construct the equation for dissociation of NaOH.	$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$ NaOH is a strong base and is completely dissociated in water.
Determine the number of moles of OH^- based on the dissociation equation.	$n(OH^-) = n(NaOH)$ $= 0.025\,mol$
Use the formula for determining concentration, given number of moles and volume: $c = \frac{n}{V}$	$n = 0.025\,mol$ $V = 0.100\,L$ $c = \frac{0.025}{0.100}$ $= 0.25\,mol\,L^{-1}$ Therefore, $[OH^-] = 0.25\,mol\,L^{-1}$
Now that you have a value for the concentration of OH^- ions, there are two ways of continuing with this problem.	

Approach 1: Calculate pOH using: $pOH = -\log_{10}[OH^-]$ Then calculate pH using: $pH + pOH = 14$	**Approach 1:** $pOH = -\log_{10}0.25$ $= -(-0.602)$ $= 0.60$ $pH = 14 - pOH$ $= 14 - 0.60$ $= 13.40$
Approach 2: Determine the $[H_3O^+]$ in the solution by substituting the $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-]$ $= 1.00 \times 10^{-14}$ Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer.	**Approach 2:** $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.25}$ $= 4.0 \times 10^{-14}\,mol\,L^{-1}$ $pH = -\log_{10}[H_3O^+]$ $= -\log_{10}4.0 \times 10^{-14}$ $= 13.40$
Both approaches are equally valid and mathematically equivalent. However, you may decide that one approach suits you more than the other.	

➤ Try yourself 3.3.4

CALCULATING pH IN A SOLUTION WHERE THE SOLUTE CONCENTRATION IS NOT GIVEN

Calculate the pH of a solution at 25°C that contains 0.50 g of potassium hydroxide (KOH) in 500 mL of solution.

Worked example 3.3.5

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate $[H_3O^+]$ in a solution of pH 5.0 at 25°C.

Thinking	Working
Determine which form of the relationship between pH and $[H_3O^+]$ should be used: $pH = -\log_{10}[H_3O^+]$ or $[H_3O^+] = 10^{-pH}$	Because you have the pH and are calculating $[H_3O^+]$, use: $[H_3O^+] = 10^{-pH}$
Substitute the value of pH into the relationship expression and use a calculator to determine the answer.	$[H_3O^+] = 10^{-pH}$ $= 10^{-5.0}$ $= 1 \times 10^{-5}\,mol\,L^{-1}$ (or $0.00001\,mol\,L^{-1}$)

➤ Try yourself 3.3.5

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate $[H_3O^+]$ in a solution of pH 10.4 at 25°C.

Effect of temperature on pH

Earlier, the ionisation constant of water was described as:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 25°C$$

You can use this relationship to calculate either $[H_3O^+]$ or $[OH^-]$ at 25°C in different solutions. But what happens if the temperature is not 25°C?

From experimental data, we know that the value of K_w increases as the temperature increases, as shown in Table 3.3.2.

The pH of pure water is only 7.00 at 25°C. At other temperatures, even though the pH of pure water is not equal to 7.00, it can still be described as neutral because the concentrations of H_3O^+ and OH^- ions are equal.

TABLE 3.3.2 The effect of temperature on pH of pure water

Temperature (°C)	K_w	pK_w	pH
0	1.14×10^{-15}	14.94	7.47
5	1.85×10^{-15}	14.73	7.37
15	4.51×10^{-15}	14.35	7.17
25	1.00×10^{-14}	14.00	7.00
35	2.09×10^{-14}	13.68	6.83
45	4.01×10^{-14}	13.40	6.70
55	7.29×10^{-14}	13.14	6.57

3.3 Review

SUMMARY

- Water self-ionises according to the equation:
  $$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
- The ionic product for water is:
  $$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 25°C$$
- The concentration of $[H_3O^+]$ is calculated using the pH scale:
  $$pH = -\log_{10}[H_3O^+]$$
- The concentration of $[OH^-]$ is calculated using the pOH scale:
  $$pOH = -\log_{10}[OH^-]$$
- The relationship between pH and pOH is given by:
  $$pH + pOH = 14.$$
- At 25°C, the pH of a neutral solution is 7.0. The pH of an acidic solution is less than 7.0 and the pH of a basic solution is greater than 7.0.
- The pH decreases when a solution of a base is diluted. The pH of a diluted base can be determined by:
  - calculating the concentration of hydroxide ions in the diluted base
  - using the ionic product of water to calculate the concentration of hydrogen ions in the diluted base.

Continued over page

3.3 Review *continued*

KEY QUESTIONS

Describe

1 Human blood has a pH of 7.4. Identify whether blood is acidic, basic or neutral.

2 Determine the pH of the following and place in order of highest pH to lowest pH:
- 0.02 M barium hydroxide
- 0.03 M NaOH
- 0.1 M HCl
- 0.08 M H_2SO_4

Apply

3 Determine the H^+ ion concentration at a pOH of 5.6.

4 Determine the pOH of a solution produced from 0.2 mole H_2SO_4 dissolved in 100 mL.

5 The pH of a cola drink is 3.0 and the pH of black coffee is 5.0. Determine how many more times acidic the cola is than the black coffee.

Analyse

6 Determine the pH of a 200 mL solution that contains 0.365 g of HCl.

7 Calculate $[OH^-]$ at 25°C in an aqueous solution in which $[H_3O^+] = 0.001\ mol\ L^{-1}$.

8 Calculate $[H_3O^+]$ at 25°C in an aqueous solution in which $[OH^-] = 1.0 \times 10^{-5}\ mol\ L^{-1}$.

9 The pH of water in a lake is 6.0. Calculate $[H_3O^+]$ in the lake.

10 This table shows the effect of temperature on the pH of pure water.

Temperature	pH
10	7.27
15	7.17
20	7.08
25	7.00
30	6.92
50	6.63

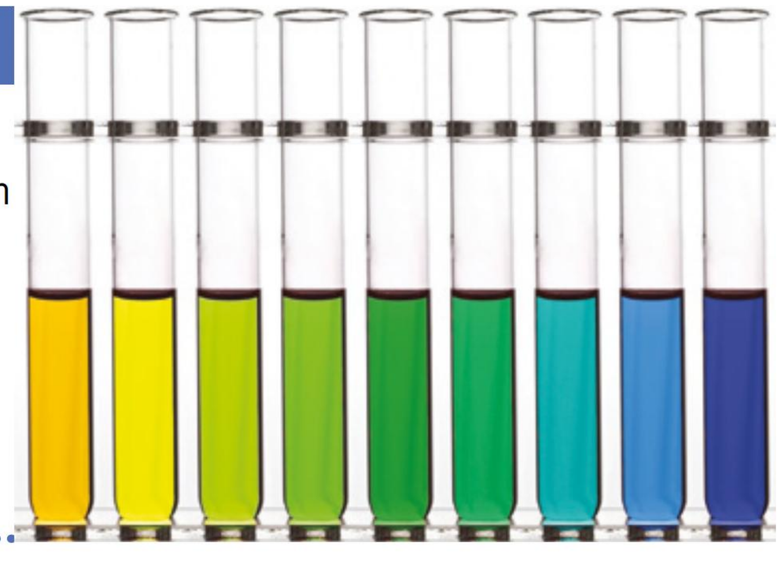
a Calculate the K_w of pure water at 50°C. Show your working.

b Analyse the data to explain whether the self-ionisation of water is endothermic or exothermic. Explain your reasoning.

3.4 Acid–base dissociation constants (K_a, K_b)

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- apply your knowledge of dissociation of acids and bases in solution to determine the strength of acids and bases at equilibrium in aqueous solution
- apply your knowledge of dissociation of acids and bases in solution to determine the expression for the dissociation constant for acid–base equilibria
- analyse experimental evidence to explain the strengths of acids and bases
- perform calculations involving acid–base dissociation constants.



ACID DISSOCIATION CONSTANTS, K_a

You will recall from Module 3.2 that a strong acid is one that fully ionises in water, forming hydronium ions and its conjugate base. A weak acid only partially ionises when reacted with water and can be represented by HA in the following equilibrium reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

The equilibrium expression for this generalised reaction is given by

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Weak acid equilibria are considered so important that the equilibrium constant is given a special name and symbol, i.e. the acid **dissociation constant**, K_a. Other common names given to the acid dissociation constant include the acidity constant and the acid ionisation constant.

In Chapter 2, you learnt that the size of the equilibrium constant indicates the extent of the reaction. In the same way, the acid dissociation constant indicates the extent of ionisation of the acid (HA) to its conjugate base (A^-).

If the value of K_a is large, the concentration of the products of the ionisation reaction is high and therefore favoured. That is, the acid ionises readily and is therefore referred to as a strong acid.

If the value of K_a is small, the acid does not readily ionise making it a weak acid.

The value of K_a for ethanoic acid is 1.75×10^{-5} at 25°C. This relatively small value means that in ethanoic acid solutions, the position of equilibrium favours the reactants and there are relatively low concentrations of products:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Ethanoic acid is classified as a weak acid because at equilibrium less than 1% of the CH_3COOH molecules in a $1.0\,mol\,L^{-1}$ solution are dissociated.

In contrast, hydrochloric acid, HCl(aq), has an acidity constant of 10^7 at 25°C. This means that the degree of ionisation for hydrochloric acid in water is almost 100%:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

Almost all of the HCl molecules have been converted to H^+ and Cl^-. Hydrochloric acid is therefore classified as a strong acid. Therefore, equilibrium arrows are not used.

The acidity constant is used as a measure of acid strength. The acid dissociation constants, K_a, of several common acids are listed in Table 3.4.1, from strongest to weakest acid. As noted above, the larger the K_a value, the stronger the acid, and you

can see, for example, that although phosphoric acid is stronger than citric acid, it is weaker than nitric acid.

Table 3.4.1 also lists the magnitudes of pK_a and you may, at times, find these values to be a useful measure of acidity. The pK_a values are calculated by applying the p-function to K_a:

$$pK_a = -\log_{10} K_a$$

Since the p-function represents a negative (or inverse) relationship, the smaller the pK_a value, the stronger the acid, as shown in the final column of Table 3.4.1.

TABLE 3.4.1 K_a values of some common acids at 25°C

Name	Formula	K_a	pK_a
hydrochloric acid	HCl	10^7	–7.00
sulfuric acid*	H_2SO_4	10^3	–3.00
nitric acid	HNO_3	2.4×10^1	1.38
phosphoric acid*	H_3PO_4	7.1×10^{-3}	2.15
citric acid*	$H_3C_6H_5O_7$	7.2×10^{-4}	3.14
hydrofluoric acid	HF	6.8×10^{-4}	3.17
nitrous acid	HNO_2	4.5×10^{-4}	3.35
methanoic acid	HCOOH	1.8×10^{-4}	3.74
ethanoic acid	CH_3COOH	1.75×10^{-5}	4.76
carbonic acid	H_2CO_3	4.3×10^{-7}	6.37
boric acid	H_3BO_3	5.9×10^{-10}	9.23

* Sulfuric acid, citric acid and phosphoric acid are polyprotic acids. The value of K_a is for the ionisation of the first proton.

K_a values for polyprotic acids

Polyprotic acids donate their protons in stages. For example, in the case of phosphoric acid, a triprotic acid, K_a decreases from the first ionisation reaction through to the third ionisation reaction.

Stage 1: $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$ $\quad K_a = 7.1 \times 10^{-3}$

Stage 2: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$ $\quad K_a = 6.3 \times 10^{-8}$

Stage 3: $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$ $\quad K_a = 4.2 \times 10^{-13}$

The first ionisation reaction occurs to a greater extent than the second. The second ionisation reaction occurs to a greater extent than the third.

In general, for polyprotic acids, it becomes harder for positively charged protons to be lost as the acid species becomes increasingly negative and K_a values decrease for each ionisation stage.

> The value of the dissociation constant, K_a, gives an indication of the strength of an acid.

BASE DISSOCIATION CONSTANTS, K_b

Weak bases are substances that act as proton acceptors and only partially ionise when dissolved in water. They interact with water by accepting protons from H_2O, resulting in the formation of OH^- ions and the conjugate acid of the base. The general reaction of a weak base, B, with water can be written as:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

The equilibrium expression for this reaction is:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

where K_b is the base dissociation constant. The most common weak base you will encounter in your chemistry studies is ammonia (NH_3). The ionisation reaction and K_b expression for the reaction between ammonia and water is:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Like K_a, the value of K_b reflects the degree of ionisation of the base when it reacts with water; the greater the value of K_b, the greater the degree of ionisation and the stronger the base. Remember, the strength of a base is a measure of how readily it accepts protons from an acid.

The base dissociation constants, K_b, of some common weak bases are shown in Table 3.4.2 in order of decreasing strength. The chemical structures of these bases includes at least one non-bonding pair of electrons on a nitrogen atom, allowing the formation of a coordinate covalent bond between the base and the proton (H^+) donated by a water molecule.

The pK_b values are also shown in the final column of Table 3.4.2, illustrating, once again, an inverse relationship—the stronger the base, the smaller the pK_b value.

TABLE 3.4.2 K_b values of some common bases at 25°C

Name	Formula	K_b	pK_b
dimethylamine	$(CH_3)_2NH$	5.1×10^{-4}	3.29
ethylamine	$C_2H_5NH_2$	4.7×10^{-4}	3.33
methylamine	CH_3NH_2	4.4×10^{-4}	3.36
ammonia	NH_3	1.8×10^{-5}	4.74
hydrazine	N_2H_4	1.7×10^{-6}	5.77
hydroxylamine	NH_2OH	1.1×10^{-8}	7.96
pyridine	CSHSN	1.4×10^{-9}	8.85
aniline	$C_6H_5NH_2$	4.2×10^{-10}	9.38
urea	NH_2CONH_2	1.5×10^{-14}	13.82

THE RELATIONSHIP BETWEEN K_a AND K_b

You have seen that a weak acid, HA, reacts with water to produce its conjugate base, A^-, and the hydronium ion, H_3O^+. This reaction and its associated K_a expression can be represented as:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq) \qquad K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

The conjugate base, A^-, is an anion of the weak acid and it acts as a weak base. When A^- reacts with water, it produces its conjugate acid, HA, and the hydroxide ion, OH^-:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq) \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

When K_a and K_b are multiplied in a conjugate acid–base equilibrium system, the product equals the ionic product of water, K_w,

$$K_a \cdot K_b = \left(\frac{[A^-][H_3O^+]}{[HA]}\right) \cdot \left(\frac{[HA][OH^-]}{[A^-]}\right) = [H_3O^+][OH^-] = K_w$$

And since K_w equals 1.0×10^{-14} at 25°C, the following relationship is established:

$$K_a \cdot K_b = K_w = 1.0 \times 10^{-14}$$

There are two important consequences of this relationship:

1. As the strength of an acid increases (larger K_a values), the strength of the conjugate base decreases (smaller K_b values) in such a way as to keep the product $K_a \cdot K_b$ constant at 1.0×10^{-14}. The reverse is also true; as the strength of

a base increases (larger K_b values), the strength of the conjugate acid decreases (smaller K_a values). You have already met this inverse relationship in Figure 3.2.4, where you noted *the stronger an acid, the weaker its conjugate base*, and *the weaker the acid, the stronger its conjugate base*.

2. This relationship allows you to calculate the K_a of any weak acid if you know the value of K_b for its conjugate base. Likewise, you can calculate the K_b of any weak base if we know the value of K_a for its conjugate acid.

As noted above, the values for K_a and K_b are often expressed in terms of pK_a and pK_b. This relationship is therefore sometimes expressed in terms of pK_a and pK_b. Taking the negative log of both sides of the equation above gives:

$$pK_a + pK_b = pK_w = 14.00 \text{ (at 25°C)}$$

Remember, these relationships only apply to acid–base systems involving conjugate pairs—such as an acid mixed with a salt of its conjugate base, or a base mixed with a salt of its conjugate acid. One of the most important applications of conjugate acid–base systems is their use in **buffer** solutions, which you will explore in the next module.

CALCULATIONS USING DISSOCIATION CONSTANTS (K_a, K_b, pK_a AND pK_b)

As you saw with equilibrium constants in Chapter 2, the equilibrium constant can be calculated from the concentrations of reactants and products in a reaction at a particular temperature. Similar calculations can be used to determine the dissociation constants (K_a or K_b) for reactions involving weak acids and bases. In addition, the equilibrium concentrations of an acid and its conjugate base (or a base and its conjugate acid) can also be determined if given the value of K_a (or K_b). Knowing equilibrium concentrations in weak acid/base equilibria also allows you to determine the pH of the final solution, which is important in many real-world applications. The following worked examples show you how.

Worked example 3.4.1

CALCULATING CONCENTRATIONS USING DISSOCIATION CONSTANTS

The concentration of CH_3COOH at 25°C is 1.00 mol L^{-1}. The value for the equilibrium constant for this reaction is 1.75×10^{-5}. Calculate the concentration of the ethanoate ion at 25°C.

Thinking	Working
Construct an equation for the ionisation reaction.	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
Formulate an expression for the dissociation constant.	$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$
Draw up an ICE table to determine the initial and final concentrations of the species present. N.B. H_2O is a pure liquid and solvent in this reaction and is therefore omitted form the K_a expression. Assume that the concentration of hydrogen ions will be x mol L^{-1} at equilibrium.	**Species** | CH_3COOH | H^+ | CH_3COO^- **Initial** | 1.00 | 0 | 0 **Change** | $-x$ | $+x$ | $+x$ **Equilibrium** | $1.00 - x$ | $+x$ | $+x$

Substitute the values in the ICE table into the dissociation constant expression.	$1.75 \times 10^{-5} = \frac{x \times x}{1.00 - x}$
Rearrange the equation to solve for x. Since x is very small, $1.00 - x$ approximates to 1.00, given the extent of ionisation of this weak acid is low.	$1.75 \times 10^{-5} = \frac{x^2}{1.00}$ $1.75 \times 10^{-5} \times 1.00 = x^2$ $x = \sqrt{1.75 \times 10^{-5}}$ $= 0.00418\,\text{mol L}^{-1}$ The concentration of the ethanoate ion (CH_3COO^-) is therefore 4.18×10^{-3} mol L^{-1}.

➤ Try yourself 3.4.1

CALCULATING CONCENTRATIONS USING DISSOCIATION CONSTANTS

The concentration of CH_3COOH at 25°C is $2.00\,\text{mol L}^{-1}$. The value for the equilibrium constant for this reaction is 1.75×10^{-5}. Calculate the concentration of the ethanoate ion at 25°C.

Worked example 3.4.2

CALCULATING THE pH OF A BASE USING THE DISSOCIATION CONSTANT

Calculate the pH of a $1.00\,\text{mol L}^{-1}$ solution of ammonia (NH_3) if the K_b for its ionisation at 25°C is 1.80×10^{-5}.

Thinking	Working
Construct an equation for the ionisation reaction.	$NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
Formulate an expression for the dissociation constant.	$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$
Substitute the values for concentration for each of the reactants and products. Because ammonia is a weak base, we can assume that it ionises to a very small extent, and the equilibrium concentration of ammonia will be the same as its initial concentration.	$1.80 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{1.00}$
Because the concentrations of NH_4^+ and OH^- will be equal at equilibrium, the equation can be simplified.	$1.80 \times 10^{-5} = \frac{[OH^-]^2}{1.00}$
Rearrange and solve for $[OH^-]$.	$1.80 \times 10^{-5} = \frac{[OH^-]^2}{1.00}$ $[OH^-]^2 = 1.80 \times 10^{-5} \times 1.00$ $[OH^-]^2 = 1.80 \times 10^{-5}$ $[OH^-] = \sqrt{1.80 \times 10^{-5}}$ $= 0.00424\,\text{mol L}^{-1}$ Therefore, $[OH^-] = 0.00424\,\text{mol L}^{-1}$

Determine $[H_3O^+]$ in the solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-]$ $= 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.00424}$ $= 2.36 \times 10^{-12}\,mol\,L^{-1}$
Use the formula $pH = -\log_{10}[H_3O^+]$ to calculate pH.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(2.36 \times 10^{-12})$ $= 11.6$

➤ Try yourself 3.4.2

CALCULATING THE pH OF A BASE USING THE DISSOCIATION CONSTANT

Calculate the pH of a $0.500\,mol\,L^{-1}$ solution of ammonia (NH_3) if the K_b for its ionisation at 25°C is 1.80×10^{-5}.

3.4 Review

SUMMARY

- The equilibrium expression for the dissociation of a monoprotic acid in water:

  $$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

  is written as $K_a = \frac{[H_3O^+][A^-]}{[HA]}$
- K_a is known as the acidity constant and is a measure of the strength of an acid.
- K_b is known as the dissociation constant for a base and is a measure of the strength of a base.

KEY QUESTIONS

Describe

1 Formulate an expression for the dissociation constant for ethanoic acid (CH_3COOH).

Apply

2 **a** Determine the strongest acid using the following information.

$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$
$K_a = 7.1 \times 10^{-3}$

$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$
$K_a = 6.3 \times 10^{-8}$

$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$
$K_a = 4.2 \times 10^{-13}$

b For each acid shown in part **a** above, calculate the equilibrium constant for the conjugate base.

Analyse

3 Calculate the pH of $0.200\,mol\,L^{-1}$ CH_3COOH that has a K_a of 1.80×10^{-5}.

4 Calculate the pH of $0.500\,mol\,L^{-1}$ $C_6H_5NH_2$ that has a K_b of 3.80×10^{-10}.

5 The hydrogen sulfate ion and the hydrogen carbonate ion are both amphiprotic, as shown by the following equations. The equilibrium constants for the reaction of these ions with water are also provided.

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$
$K_a = 1.0 \times 10^{-2}$

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_2SO_4(aq) + OH^-(aq)$
$K_b = 1.0 \times 10^{-12}$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$
$K_a = 4.7 \times 10^{-11}$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$
$K_b = 2.1 \times 10^{-4}$

Using the K_a of these solutions, determine which of the above is the strongest acid.

6 The table below shows the K_a value for several acids.

Acid	K_a (20°C)
ethanoic acid	1.8×10^{-5}
chlorous acid	1.1×10^{-2}
nitrous acid	4.0×10^{-4}
phosphoric acid	7.5×10^{-3}

a Sequence the acids in order of weakest to strongest.

b What is the concentration of a nitrous acid solution with a pH of 3.1. Nitrous acid is monoprotic.

7 Determine the concentration of a barium hydroxide solution with a pH of 12.7.

3.5 Buffers

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that solutions known as buffers resist a change in pH when a small amount of acid or base is added to the solution
- understand how Le Châtelier's principle can be applied to predict how buffer solutions respond to the changes in concentration of acid or base in the solution.

THE CONJUGATE NATURE OF BUFFERS

Buffers are solutions that resist changes in pH when small amounts of an acid or base are added. They typically consist of a weak acid and its conjugate base, or a weak base and its conjugate acid. Buffers play a critical role in stabilising pH in chemical reactions, including biochemical processes in living organisms, natural water systems (such as oceans, rivers and lakes) and a wide range of industrial processes.

Until now, you have considered acid–base equilibria that involve only a weak acid or only a weak base. For example, the equilibrium reaction of the weak acid, ethanoic acid, is given by:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

This equilibrium mixture contains the acid (CH_3COOH) and its conjugate base (CH_3COO^-). However, since CH_3COOH ionises only slightly in water, the amount of the conjugate base present in the equilibrium mixture is relatively small.

To create a buffer solution using ethanoic acid, additional ethanoate ions are deliberately introduced by adding a salt such as sodium ethanoate ($NaCH_3COO$). This ensures the equilibrium mixture contains appreciable amounts of both the acid (CH_3COOH) and its conjugate base (CH_3COO^-).

Buffers resist changes in pH because they contain appreciable amounts of both an acidic species (to neutralise added OH^-) and a basic species (to neutralise added H_3O^+). These acidic and basic species must not consume each other in the type of neutralisation reaction you encountered in Unit 2 (e.g. $HCl + NaOH \rightarrow NaCl + H_2O$). This is why buffers are prepared using an acid–base conjugate pair.

BUFFERS AND LE CHATELIER'S PRINCIPLE

You will remember from Chapter 2 that Le Châtelier's principle states that a system at equilibrium will act to partially oppose the effects of a change to the equilibrium reaction conditions. To understand how this principle applies to buffers, consider a system of a weak monoprotic acid (HA) with one of its salts (MA), where M is a singly charged cation (such as Na^+ or K^+). The equilibrium mixture contains appreciable amounts of both the acid, HA, and its conjugate base, A^-. The relevant equilibrium equation is:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

This equilibrium contains an acid on the left-hand side of the equation and a base on the right-hand side of the equation. When a small amount of acid (H_3O^+ ions) is added to the buffered solution, it reacts with the base component (A^-) to produce the acid component (HA), i.e. the added acid is neutralised:

$$A^-(aq) + H_3O^+(aq) \rightarrow HA(aq) + H_2O(l)$$

When a small amount of base (OH^- ions) is added to the buffered solution, it reacts with the acid component (HA) to produce the base component (A^-), i.e. the added base is neutralised:

$$HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(l)$$

As long as the buffer contains sufficient amounts of both HA and A^-, it can resist major shifts in the equilibrium position by neutralising added H_3O^+ or OH^-, thereby resisting pH changes.

OTHER BUFFER SYSTEMS

The buffer system described above, employing ethanoic acid and the ethanoate ion, is an example of an acidic buffer. Acidic buffers are used to maintain stable pH values below 7 and typically consist of a weak acid and its conjugate base. In contrast, a basic buffer is prepared from a weak base and its conjugate acid, stabilising solutions with pH values above 7. A buffer consisting of the weak base ammonia (NH_3) and an ammonium salt (such as ammonium chloride, NH_4Cl) is an example of a basic buffer. Ammonium salts contain the NH_4^+ ion, which is the conjugate acid of NH_3. Therefore, the relevant equilibrium equation is:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Buffers that resist pH changes at around neutral pH values (~pH 7) are important for many biomedical applications. One commonly used buffer for this purpose is the phosphate buffer system, consisting of the hydrogen phosphate ion (HPO_4^{2-}) and its conjugate acid, the dihydrogen phosphate ion ($H_2PO_4^-$). This buffer works by neutralising small additions of acids and bases using the following equilibrium reaction:

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$$

When acid is added, HPO_4^{2-} reacts with H_3O^+ to from $H_2PO_4^-$:

$$HPO_4^{2-}(aq) + H_3O^+(aq) \rightarrow H_2PO_4^-(aq) + H_2O(l)$$

When a base is added, $H_2PO_4^-$ reacts with OH^- to from HPO_4^{2-}:

$$H_2PO_4^-(aq) + OH^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(l)$$

In all cases, the addition of small amounts of acid or base shifts the position of equilibrium slightly, counteracting the impact of the change in accordance with Le Châtelier's principle.

3.5 Review

SUMMARY

- Buffer solutions are those that resist a change in pH when a small amount of acid or base is added to them.
- An acidic buffer solution can be formed by combining a weak acid with a salt of the acid.
- An alkaline buffer solution can be formed by combining a weak base with a salt of the base.

KEY QUESTIONS

Describe

1 Define 'buffer'.

Apply

2 Describe the relationship between ammonia and its conjugate acid (NH_4^+) when a small amount of sodium hydroxide (NaOH) is added to the solution.

3 Explain why hydrochloric acid is not a suitable acid for use in preparing a buffer solution.

Analyse

4 Determine what will happen to the pH of a sodium ethanoate buffer solution if concentrated HCl solution is continually added to it.

5 Predict how a buffer solution, consisting of carbonic acid (H_2CO_3) and hydrogen carbonate ions would react to resist a change in pH when a small amount of hydrochloric acid is added.

$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \rightleftharpoons CO_3^{2-}(aq) + 2H^+(aq)$

In your answer, describe the change to the equilibrium and the effect on the concentration of CO_3^{2-}.

Chapter review

03

KEY TERMS

acid
acid–base reaction
acidic proton
acidic solution
acidity
acidity constant
amphiprotic
base
basicity
basic solution
Brønsted–Lowry model
buffer
concentrated solution
concentration
conjugate acid
conjugate acid–base pair
conjugate base
dissociate
dissociation
dissociation constant
hydrogen ion
hydronium ion
hydroxide ion
ionic product of water
ionisation
ionisation constant of water
ionise
monoprotic acid
neutral solution
pH scale
pOH scale
polyprotic acid
salt
self-ionisation
solute
strong acid
strong base
triprotic acid
weak acid
weak base

KEY QUESTIONS

Describe

1 Solution X has a pH of 4 and solution Y has a pH of 7. This indicates that X is

A less acidic than Y and has 0.5 times the concentration of $[H^+]$ ions in solution Y.
B more acidic and has three times the concentration of $[H^+]$ ions in solution Y.
C more acidic and has 1000 times the concentration of $[H^+]$ ions in solution Y.
D less acidic and has 0.001 times the concentration of $[H^+]$ ions in solution Y.

2 Select the reaction representing the reaction of a strong acid with water.

A $LiOH(aq) \rightarrow Li^+(aq) + OH^-(aq)$
B $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
C $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$
D $NH_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_4^-(aq)$

3 Identify what $[H_3O^+]$ in a solution is at 25°C with $[OH^-]$ equal to $2.84 \times 10^{-2}\,mol\,L^{-1}$.

A $3.98\,mol\,L^{-1}$
B $10.5\,mol\,L^{-1}$
C $2.84 \times 10^{12}\,mol\,L^{-1}$
D $3.52 \times 10^{-13}\,mol\,L^{-1}$

4 Identify what $[OH^-]$ in a solution is at 25°C with $[H_3O^+]$ equal to $5.70 \times 10^{-9}\,mol\,L^{-1}$.

A $8.3\,mol\,L^{-1}$
B $2.46\,mol\,L^{-1}$
C $5.70 \times 10^{6}\,mol\,L^{-1}$
D $1.75 \times 10^{-6}\,mol\,L^{-1}$

5 A weak acid, HA symbolising a buffer component, ionises in water according to the equation:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

Select which one of the following correctly identifies the direction of the equilibrium shift and change to A^- concentration when a small amount of NaOH is added.

A left, increase
B left, decrease
C right, increase
D right, decrease

6 Identify the reactant that acts as an acid in each of the following reactions.

a $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
b $NH_4^+(aq) + H_2O(l) \rightarrow NH_3(aq) + H_3O^+(aq)$
c $HCO_3^-(aq) + OH^-(aq) \rightarrow H_2O(l) + CO_3^{2-}(aq)$
d $SO_4^{2-}(aq) + H_3O^+(aq) \rightarrow HSO_4^-(aq) + H_2O(l)$
e $CO_3^{2-}(aq) + CH_3COOH(aq) \rightarrow HCO_3^-(aq) + CH_3COO^-(aq)$

7 Show the formula for the conjugate of:

a the acid HCl
b the base OH^-
c the base O^{2-}
d HSO_4^- when it acts as an acid.

8 Identify which of the following reactions are Brønsted–Lowry acid–base reactions.

A $HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$
B $CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$
C $2HNO_3(aq) + Mg(s) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$
D $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

Apply

9 Construct balanced equations to show that in water:

a PO_4^{3-} acts as a base
b $H_2PO_4^-$ acts as an amphiprotic substance
c H_2S acts as an acid.

10 Construct an equation to show that perchloric acid ($HClO_4$) acts as a strong acid in water.

11 Construct an equation to show that hypochlorous acid (HClO) acts as a weak acid in water.

Analyse

12 Calculate $[OH^-]$ at 25°C in aqueous solutions with $[H_3O^+]$ equal to:

- **a** $0.001\,mol\,L^{-1}$
- **b** $10^{-5}\,mol\,L^{-1}$
- **c** $5.7 \times 10^{-9}\,mol\,L^{-1}$
- **d** $3.4 \times 10^{-12}\,mol\,L^{-1}$
- **e** $6.5 \times 10^{-2}\,mol\,L^{-1}$
- **f** $2.23 \times 10^{-13}\,mol\,L^{-1}$.

13 Calculate the concentration of these ions in solutions, at 25°C, with the following pH values.

- **i** hydrogen ions
- **ii** hydroxide ions

- **a** 1
- **b** 3
- **c** 7
- **d** 11.7

14 Calculate the concentration of H^+ and OH^- ions in solutions, at 25°C, with the following pH values.

- **a** 3.0
- **b** 10.0
- **c** 8.5
- **d** 5.8
- **e** 9.6
- **f** 13.5

15 The pH of tomato juice is 5.3 at 25°C. Calculate the concentration of hydroxide ions in tomato juice.

16 A solution of hydrochloric acid has a pH of 2.0.

- **a** Calculate the molar concentration of hydrogen ions in the solution.
- **b** Calculate the number of moles of hydrogen ions that would be present in 500 mL of this solution.

17 Calculate the pH of each of the following mixtures at 25°C.

- **a** 10 mL of $0.025\,mol\,L^{-1}$ HCl is diluted to 50 mL of solution.
- **b** 20 mL of $0.005\,mol\,L^{-1}$ KOH is diluted to 500 mL of solution.
- **c** 10 mL of $0.15\,mol\,L^{-1}$ HCl is diluted to 1.5 L of solution.

18 The molarity of concentrated sulfuric acid is $18.0\,mol\,L^{-1}$. Calculate the volume of concentrated sulfuric acid required to prepare a 1.00 L solution of $2.00\,mol\,L^{-1}$ H_2SO_4.

19 When a 10.0 mL solution of hydrochloric acid is diluted, the pH changes from 2.0 to 4.0. Determine the volume of water that is added to the acid solution.

20 40.0 mL of $0.10\,mol\,L^{-1}$ HNO_3 is diluted to 500 mL. Describe the effect this would have on the pH.

21 Determine the effect on the pH of a monoprotic acid solution of pH 0.1 when it is diluted by a factor of 10.

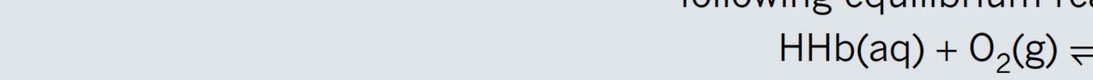
22 Calculate the pH of the base $C_6H_5NH_2$ of $0.800\,mol\,L^{-1}$, which has a K_b of 3.80×10^{-10}.

23 The concentration of CH_3COOH at 25°C is $0.500\,mol\,L^{-1}$. The value for the equilibrium constant for this reaction is 1.75×10^{-5}. Calculate the concentration of the ethanoate ion at this temperature.

Interpret

24 Explain what a high K_a value of an acid indicates in terms of the position of equilibrium and whether it is a potential acid for use in a buffer.

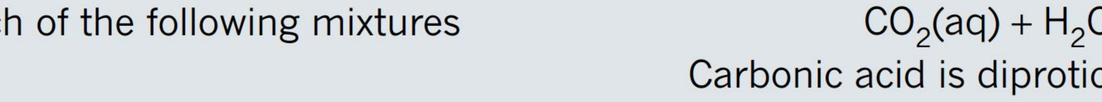
25 Haemoglobin binds to oxygen in the blood, enabling oxygen to be transported around the body and deposited in tissues and cells where it is needed. This is a reversible process that can be represented by the following equilibrium reaction:



$$HHb(aq) + O_2(g) \rightleftharpoons H^+(aq) + HbO_2^-(aq)$$

The human body, particularly the bloodstream, requires buffering systems to control the level of acidity to ensure that biological reactions take place at an optimum rate. Determine why these buffering systems are necessary given the above reaction, using Le Châtelier's principle and your knowledge of pH.

26 Carbon dioxide is slightly soluble in water. As levels of carbon dioxide in the atmosphere are increasing, more carbon dioxide is dissolving into the oceans. Some of this carbon dioxide remains as $CO_2(aq)$, but some reacts further to produce carbonic acid in the following reaction:



$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Carbonic acid is diprotic, meaning it can dissociate in two stages.

- **a** Construct equations for these two stages.
- **b** Determine what effect more CO_2 released from the burning of fossil fuels has on the position of equilibrium in each reaction.
- **c** Explain the effect of this in terms of pH.
- **d** Since the beginning of the Industrial Revolution, the pH of the oceans has decreased by 0.11 units. Calculate the change in H_3O^+ concentration in this time.

Data analysis

DATA SET 1

The information below applies to Questions 1–5.

The table gives the properties of four monoprotic acids.

Acid	Concentration (mol L^{-1})	$[H^+]$	pH	K_a
$CH_3COOH(aq)$	0.1			1.78×10^{-5}
HCl(aq)	0.1	1.00×10^{-1}	1.00	>1
unknown acid 1	0.2	7.90×10^{-5}		
unknown acid 2	0.1	4.20×10^{-3}	2.34	1.80×10^{-4}

Question 1 (2 marks)

Using HCl data as an example, describe the relationship between $[H^+]$ and pH of a solution.

Question 2 (2 marks)

Calculate the K_a for unknown acid 1.

Question 3 (2 marks)

Write a chemical equation for the ionisation of CH_3COOH (in water).

Question 4 (2 marks)

Identify whether the conjugate base of ethanoic acid ($CH_3COOH(aq)$) is amphiprotic. Explain your reasoning.

Question 5 (2 marks)

Calculate the pH of the aqueous solution of ethanoic acid. Show your working.

CHAPTER 04

Volumetric analysis

There are many situations in which a chemist may want to find the amount of a substance in solution, such as the amount of a chemical present in industrial or mining wastes, the composition of antacid tablets or the acidity of polluted rainwater.

This chapter describes a method used for the analysis of acids and bases in water. The method is called volumetric analysis and involves chemical reactions between substances in aqueous solution.

Volumetric analysis requires the measurement of accurate volumes using specialised pieces of glassware. By the end of this chapter, you will have a greater understanding about the use of this glassware in a process known as a titration. You will learn how titration data are used to calculate the concentration of an acid or a base in an aqueous solution. You will also learn that acid–base indicators are weak acids that are one colour in their acid form and a different colour in their conjugate base form, and how this colour change is used in a titration. Finally, you will learn about the features of titration curves and how this data are used to select a suitable acid–base indicator for a titration.

Syllabus subject matter

Topic 1 • Chemical equilibrium systems

VOLUMETRIC ANALYSIS

- Discriminate between the terms end point and equivalence point. **4.2, 4.3**
- Sketch the general shapes of conductometric and acid–base titration curves involving strong and weak acids and bases. (Titration of weak acids to weak bases is not required.) **4.4**
- Interpret acid–base titration curves to determine the intercept with pH axis, equivalence point, buffer region and points where pK_a = pH or pK_b = pOH. **4.4**
- Interpret conductometric titration curves to determine the intercept with conductivity axis, equivalence point and volume of titrant. **4.4**
- Analyse volumetric data, including solubility, conductometric and acid–base titration curves, to determine moles, mass, volume and concentration. **4.1, 4.2, 4.4**
- Analyse titration curves to calculate the concentration of a solution with reference to a standard solution. **4.3, 4.4**

ACID–BASE INDICATORS

- Identify that acid–base indicators are a weak acid or a weak base where the conjugate acid–base pair have different colours and can be represented by $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$ or $BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$. **4.3**
- Identify that indicators change colour when pH = pKa. **4.3**
- Explain the relationship between the pH range, the end point and the pKa value of an acid–base indicator. **4.3**
- Analyse data to determine an appropriate indicator given the equivalence point of the titration and the pH range of the indicator (assuming indicators change colour over a range of pKa ± 1). **4.3, 4.4**

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4.1 Principles of volumetric analysis

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- explain how standard solutions can be prepared
- use stoichiometry to determine unknown concentrations of acids and bases.

Volumetric analysis is a common technique used by analytical chemists, and it will be the focus of this chapter. Volumetric analysis can be used to accurately determine the concentration of acids and bases in solution. This technique involves the reaction between a solute of unknown concentration in one solution and a solute of accurately known concentration in a second solution. In this module, you will learn how to prepare a solution with an accurately known concentration and then use this concentration and stoichiometry to calculate the unknown concentration of a solution.

STANDARD SOLUTIONS

A **standard solution** is a solution in which the concentration of the solute is accurately known. Pure substances that are widely used in the laboratory to prepare solutions of accurately known concentrations are called **primary standards**.

Primary standards are substances that are so pure that the number of moles of a substance can be calculated accurately from its mass.

A primary standard should:

- be readily obtainable in a pure form
- have a known chemical formula
- be easy to store without deteriorating or reacting with the atmosphere
- have a high molar mass to minimise the effect of errors in weighing
- be inexpensive.

Examples of primary standards are:

- acids: hydrated oxalic acid ($C_2H_2O_4{\cdot}2H_2O$) and potassium hydrogen phthalate ($KH(C_8H_4O_4)$)
- bases: anhydrous sodium carbonate (Na_2CO_3) and sodium borate ($Na_2B_4O_7{\cdot}10H_2O$).

Remember that the term 'anhydrous' indicates there is no water present in the compound. For example, a sample of sodium carbonate may contain water molecules incorporated into the crystal lattice structure. Anhydrous sodium carbonate is obtained by heating the sodium carbonate to above 100°C to remove any water. Storage in a desiccator prevents further absorption of water from the atmosphere.

Standard solutions are prepared by dissolving an accurately measured mass of a primary standard and adding enough water to produce an accurately measured volume of solution.

Digital balances are used in analytical laboratories to accurately weigh primary standards. The two types of balances commonly used can be seen in Figure 4.1.1. A top-loading balance can weigh to an accuracy of between 0.1 g and 0.001 g, depending on the model. Analytical balances can weigh to an accuracy of between 0.0001 g and 0.00001 g.

A **volumetric flask** or standard flask, as shown in Figure 4.1.2, is used to prepare a solution that has an accurately known volume. Volumetric flasks of 50.00 mL, 100.00 mL and 250.00 mL are frequently used in the laboratory.

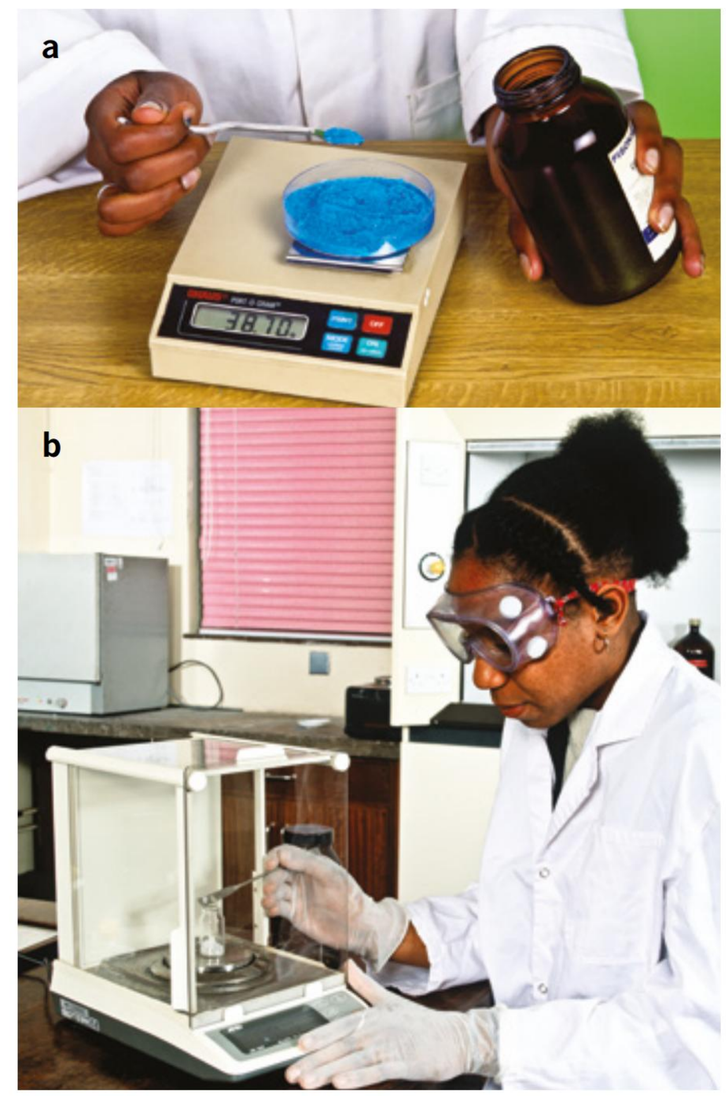


FIGURE 4.1.1 (a) A top-loading balance. (b) An analytical balance can be used to accurately weigh substances used in chemical analysis.

FIGURE 4.1.2 Volumetric flasks of various sizes are used to prepare standard solutions.

FIGURE 4.1.3 This close-up view of the neck of a standard flask shows the bottom of the meniscus level with the graduation line.

A volumetric flask is filled so that the bottom of the meniscus is level with the graduation line on the neck of the flask. This can be seen in Figure 4.1.3. Your eye should be level with the line to avoid **parallax errors** (errors caused by the shift in the apparent position of an object due to the viewing angle).

To prepare a standard solution from a primary standard, you need to dissolve an accurately known amount of the substance in deionised water to produce a solution of known volume. The steps in this process are shown in Figure 4.1.4.

The molar concentration of the standard solution is then found using these formulas:

$$\text{number of moles, } n = \frac{\text{mass of solute (in g)}}{\text{molar mass (in g mol}^{-1})} = \frac{m}{M}$$

$$\text{concentration, } c = \frac{\text{number of moles of solute (mol)}}{\text{volume of solution (L)}} = \frac{n}{V} = \frac{m}{M \times V}$$

In practice, making a standard solution directly from a primary standard is only possible for a few of the chemicals found in the laboratory. Many chemicals are impure, while others can decompose or react with chemicals in the atmosphere. For example, strong bases such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) absorb water and react with carbon dioxide in the air, and many hydrated salts such as sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) lose water to the atmosphere over time.

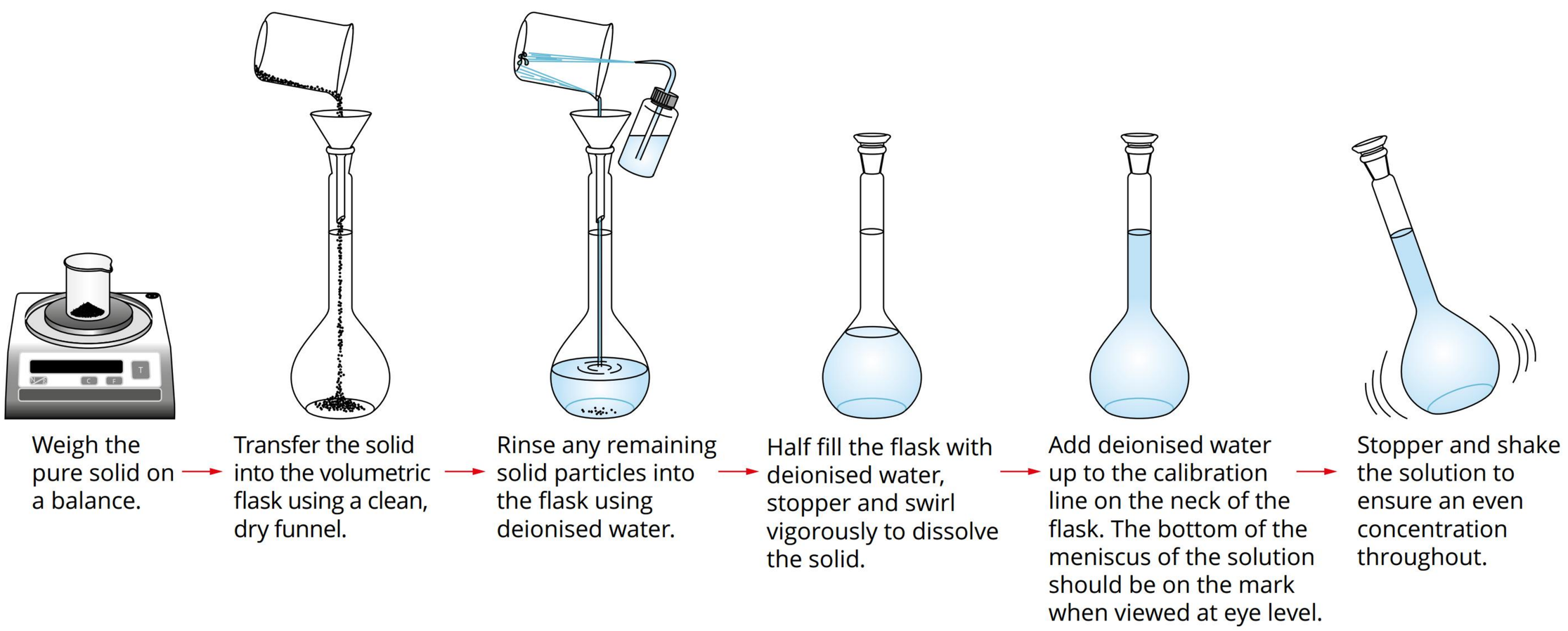


FIGURE 4.1.4 Preparing a standard solution from a primary standard

In addition, the concentrations of commercial supplies of strong acids (e.g. HCl, H_2SO_4 and HNO_3) cannot be accurately specified.

Solutions such as HCl(aq), H_2SO_4(aq), NaOH(aq) and KOH(aq) must be **standardised** to determine the concentration of solute. An accurately measured volume of the solution is reacted with a known amount of a standard solution such as anhydrous sodium carbonate, Na_2CO_3(aq), or potassium hydrogen phthalate, $KH(C_8H_4O_4)$(aq). This is done by titration, which is discussed in Module 4.2.

Concentration of standard solutions

In Unit 2, you learnt how to calculate the concentration of a solution and determine the amount of solute required to prepare a solution of a specific concentration.

Figure 4.1.5 summarises the steps involved in calculating the concentration of solute in a standard solution from the accurately measured mass of a primary standard.

A standard solution is a solution in which the concentration of solute is accurately known.

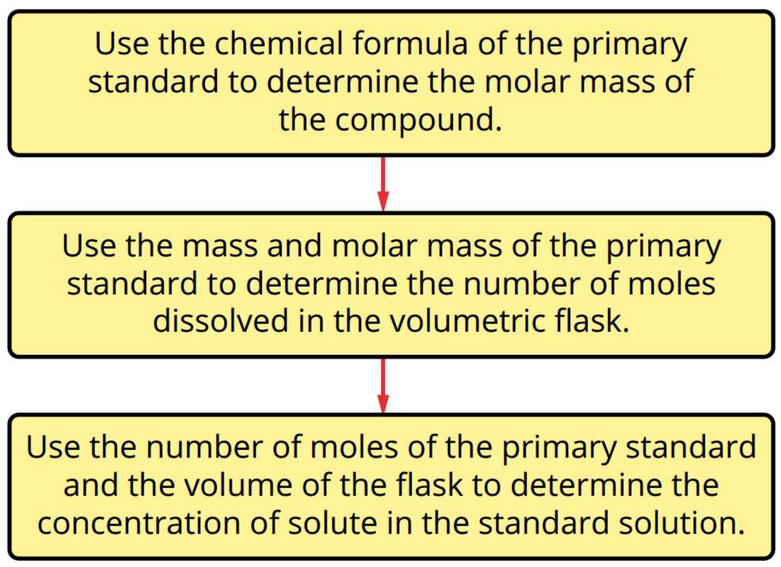


FIGURE 4.1.5 A summary of the steps used in the calculation of the concentration of solute in a standard solution prepared from a primary standard

Worked example 4.1.1

CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD

Calculate the concentration of a standard solution prepared from 29.22 g of sodium chloride (NaCl) dissolved in a 1.00 L volumetric flask.

Thinking	Working
Use the chemical formula to determine the molar mass (M) of the compound.	The molar mass (M) of NaCl is $22.99 + 35.45 = 58.44\,\text{g mol}^{-1}$.
Use the mass (m) and molar mass (M) of the compound and the formula $n = \frac{m}{M}$ to determine the number of moles.	$n = \frac{29.22}{58.44}$ $= 0.5000\,\text{mol}$
Use the number of moles to determine the concentration of the solution, using the formula $c = \frac{n}{V}$. Remember, volume is in L. Express your answer to the appropriate number of significant figures.	$c = \frac{0.5000}{1.00}$ $= 0.500\,\text{mol L}^{-1}$

➤ Try yourself 4.1.1

CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD

Calculate the concentration of a standard solution prepared from 117.00 g of sodium chloride (NaCl) dissolved in a 500.00 mL volumetric flask.

SOLUTION STOICHIOMETRY

When a volumetric analysis is carried out in the laboratory, calculations using the experimental data involve determining the number of moles of the reactants. Such calculations are referred to as examples of **solution stoichiometry**.

Reacting quantities of acids and bases

Calculations based on the reactions of acids usually involve determining the number of moles of a substance.

You will recall from Unit 2 that:

- the coefficients in a balanced chemical equation give the ratio in which substances react
- the number of moles of solid can be calculated from the expression $n = \frac{m}{M}$, where m is the mass in grams and M is the molar mass in $g\,mol^{-1}$
- the number of moles of solute in a solution is given by $n = cV$, where c is the concentration in $mol\,L^{-1}$ (M) and V is the volume in litres (L).

As you will see in Worked examples 4.1.2 and 4.1.3, there are four main steps in solving calculation problems involving solutions of acids and bases:

1. Write a balanced equation for the reaction.
2. Calculate the number of moles of the substance with known volume and concentration.
3. Use the ratios of the stoichiometric coefficients of reactants and products from the balanced equation to calculate the number of moles of the required substance.
4. Calculate the required volume or concentration to the correct number of significant figures.

The steps in a stoichiometric calculation can be summarised in the flow chart in Figure 4.1.6.

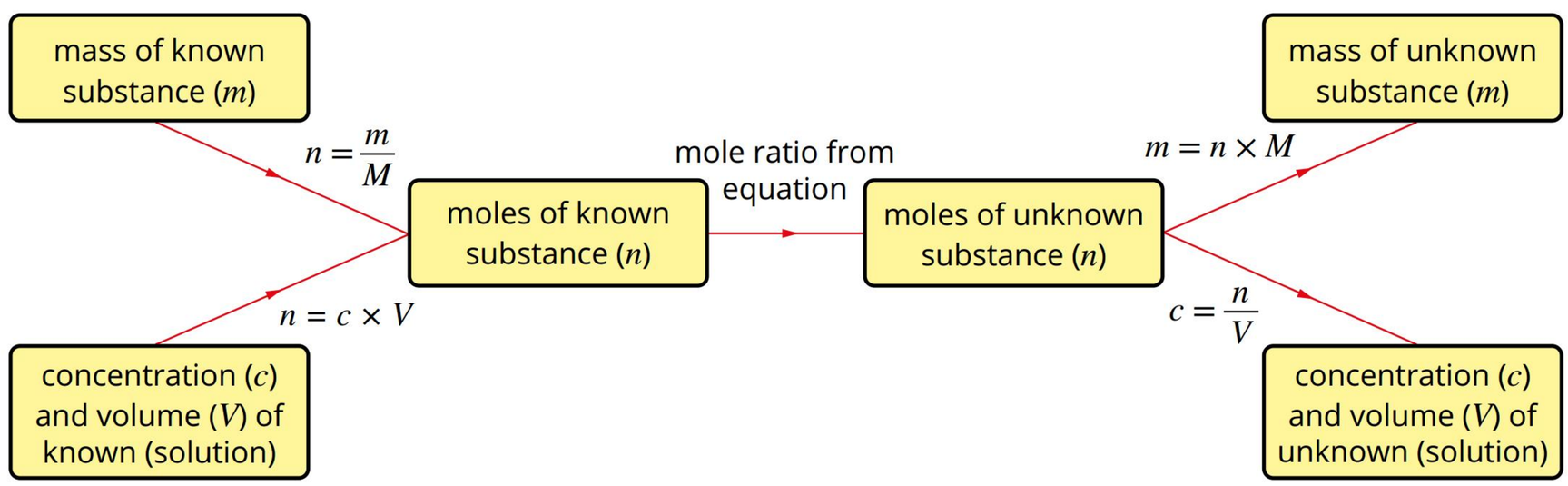


FIGURE 4.1.6 Flow chart for mass and solution stoichiometry calculations

Worked example 4.1.2

A SOLUTION STOICHIOMETRY CALCULATION

Calculate the volume of 0.100 $mol\,L^{-1}$ sulfuric acid (H_2SO_4) that reacts completely with 17.8 mL of 0.150 $mol\,L^{-1}$ potassium hydroxide (KOH) solution.	
Thinking	**Working**
Write a balanced full equation for the reaction.	$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$
Calculate the number of moles of the substance with known volume and concentration.	The volume and concentration of potassium hydroxide solution are given, so you can use $n = cV$ (remember that volume must be expressed in litres). $n(KOH) = cV$ $= 0.150 \times 0.0178$ $= 0.00267$ mol

Use the reactant coefficients in the balanced equation to calculate the number of moles of the required substance.	The balanced equation shows that 1 mole of sulfuric acid reacts with 2 mole of potassium hydroxide. $\frac{n(H_2SO_4)}{n(KOH)} = \frac{1}{2}$ $n(H_2SO_4) = \frac{1}{2} \times n(KOH)$ $= \frac{1}{2} \times 0.00267$ $= 0.00134\,mol$
Calculate the volume or concentration required.	The volume of H_2SO_4 is found by using $n = cV$. $V(H_2SO_4) = \frac{n}{c}$ $= \frac{0.00134}{0.100}$ $= 0.0134\,L = 13.4\,mL$

➤ Try yourself 4.1.2

A SOLUTION STOICHIOMETRY CALCULATION

Calculate the volume of 0.500 mol L^{-1} hydrochloric acid (HCl) that reacts completely with 25.0 mL of 0.100 mol L^{-1} calcium hydroxide ($Ca(OH)_2$) solution. The salt formed in this acid–base reaction is calcium chloride.

Stoichiometry problems involving excess reactants

Reactants are not always mixed in stoichiometric amounts in acid–base reactions. There are occasions when one of the reactants, an acid or a base, is in excess. You learnt how to determine the excess and limiting reactants in a reaction in Unit 2. The same principles for identifying the excess and limiting reactants in stoichiometric problems involving acid and base solutions apply:

- Calculate the number of moles of each reactant.
- Determine which is the **excess reactant** and which is the **limiting reactant**.
- Use the number of moles of the limiting reactant to work out the number of moles of product formed or the number of moles of reactant in excess.

Worked example 4.1.3

SOLUTION STOICHIOMETRY—A LIMITING REACTANT PROBLEM

20.0 mL of a 1.00 mol L^{-1} solution of lithium hydroxide (LiOH) is added to 30.0 mL of a 0.500 mol L^{-1} solution of nitric acid (HNO_3). The equation for the reaction that occurs is:

$HNO_3(aq) + LiOH(aq) \rightarrow LiNO_3(aq) + H_2O(l)$

a Determine the limiting reactant.

b Calculate the mass of lithium nitrate, $LiNO_3$, produced by this reaction.

a Determine the limiting reactant.

Thinking	Working
Calculate the number of moles of each of the reactants using $n = cV$. Remember to convert mL to L.	$n(HNO_3) = 0.500 \times 0.030$ $= 0.0150\,mol$ $n(LiOH) = 1.00 \times 0.020$ $= 0.0200\,mol$
Use the coefficients of the equation to find the limiting reactant.	The equation shows that 1 mole of HNO_3 reacts with 1 mole of LiOH. So, the HNO_3 is the limiting reactant (it will be completely consumed).

b Calculate the mass of lithium nitrate, $LiNO_3$, produced by this reaction.	
Thinking	**Working**
Find the mole ratio of the unknown substance to the limiting reactant from the equation coefficients: $\frac{\text{coefficient of unknown}}{\text{coefficient of limiting reactant}}$	From the equation coefficients: $\frac{n(LiNO_3)}{n(HNO_3)} = \frac{\text{coefficient of } LiNO_3}{\text{coefficient of } HNO_3} = \frac{1}{1}$
Calculate the number of moles of the unknown substance using the initial mole of the limiting reactant: $n(\text{unknown}) = n(\text{limiting reactant}) \times \text{mole ratio}$	$n(LiNO_3) = n(HNO_3) \times \frac{1}{1}$ $= 0.015 \times \frac{1}{1}$ $= 0.015\,\text{mol}$
Calculate the mass of the unknown substance using: $m(\text{unknown}) = n(\text{unknown}) \times \text{molar mass}$	Molar mass of $LiNO_3 = 68.95\,\text{g mol}^{-1}$ $m(LiNO_3) = 0.015 \times 68.95$ $= 1.03\,\text{g}$

➤ Try yourself 4.1.3

SOLUTION STOICHIOMETRY—A LIMITING REACTANT PROBLEM

30.0 mL of a 0.100 mol L^{-1} solution of sulfuric acid (H_2SO_4) is added to 40.0 mL of a 0.200 mol L^{-1} solution of potassium hydroxide (KOH). The equation for the reaction that occurs is:

$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$

a Determine the limiting reactant.

b Calculate the mass of K_2SO_4 produced by this reaction.

4.1 Review

SUMMARY

- A substance is suitable for use as a primary standard if it:
  - is readily obtainable in a pure form
  - has a known chemical formula
  - is easy to store without deteriorating or reacting with the atmosphere
  - has a high molar mass to minimise the effect of errors in weighing
  - is inexpensive.
- A standard solution is a solution in which the concentration of the solute is accurately known.
- The concentration of solute, in mol L^{-1}, of a prepared standard solution can be determined by measuring the mass of solute dissolved and the volume of solution prepared.
- Given the quantity of one of the reactants or products in a chemical reaction, the quantity of all other reactants and products can be predicted by working through the following steps.
  1. Write a balanced equation for the reaction.
  2. Calculate the number of moles of the given substances.
  3. Use the ratios of the stoichiometric coefficients of reactants and products from the balanced equation to calculate the number of moles of the required substance.
  4. Convert the number of moles of the required substance to the quantity required in the question.

- If quantities of more than one reactant are provided for a chemical reaction, the limiting reactant must be identified and used in the stoichiometry calculations.
- The limiting reactant is the reactant that is completely consumed in the reaction.
- The reactant that is not completely consumed when the reaction is complete is said to be in excess, and some of it will remain, unreacted, in the reaction mixture.

KEY QUESTIONS

Describe

1 Explain the difference between a standard solution and a primary standard.

2 Describe the steps required for the preparation of a standard solution.

3 Determine the number of moles of sodium sulfate produced when 3 moles of sodium hydroxide react with excess sulfuric acid according to the equation:
$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

Apply

4 **a** List the criteria that are used to determine if a substance is suitable for use as a primary standard.
b Identify one criterion from part a that may not be met every time a primary standard is selected for use in the laboratory. Justify your answer.

5 Determine the volume of 0.200 mol L^{-1} KOH required to react with 30.0 mL of 0.100 mol L^{-1} HNO_3.

6 Explain why NaOH is not suitable for use as a primary standard in the titration of a strong acid.

Analyse

7 Potassium hydrogen phthalate ($KH(C_8H_4O_4)$) is used as a primary standard for the analysis of bases. Calculate the concentration of a standard solution prepared in a 50.00 mL volumetric flask by dissolving 2.042 g of potassium hydrogen phthalate in deionised water. The molar mass of $KH(C_8H_4O_4)$ is 204.23 g mol^{-1}.

8 Determine the mass of anhydrous sodium carbonate (Na_2CO_3) required to prepare 250.0 mL of a 0.5000 mol L^{-1} standard solution.

9 A 0.100 mol L^{-1} solution of sulfuric acid, H_2SO_4, is neutralised with 10.0 mL of a 0.300 mol L^{-1} solution of potassium hydroxide, KOH.
a Write a balanced chemical equation for the reaction between sulfuric acid and potassium hydroxide.
b Determine the volume of sulfuric acid that was neutralised.

10 15.0 mL of a nitric acid, HNO_3, solution is required to react completely with 10.0 mL of a 0.100 mol L^{-1} solution of calcium hydroxide, $Ca(OH)_2$.
a Write a balanced chemical equation for the reaction between nitric acid and calcium hydroxide.
b Determine the concentration of the nitric acid solution.

11 125 mL of a 1.05 mol L^{-1} solution of potassium hydroxide, KOH, is mixed with 32.5 mL of a 2.15 mol L^{-1} solution of phosphoric acid and allowed to react according to the equation:
$3KOH(aq) + H_3PO_4(aq) \rightarrow K_3PO_4(aq) + 3H_2O(l)$
a Determine the limiting reactant.
b Calculate the mass of potassium phosphate, K_3PO_4, produced by this reaction.

12 A standard solution of sodium carbonate is prepared by adding 1.187 g of Na_2CO_3 to a 250.00 mL volumetric flask and filling to the calibration line with deionised water. A 25.00 mL sample of this standard solution is then reacted with 15.50 mL of a 0.125 mol L^{-1} solution of hydrochloric acid (HCl).
a Calculate the concentration of the sodium carbonate solution.
b Write a balanced chemical equation for the reaction between the hydrochloric acid and sodium carbonate solutions.
c Determine the limiting reactant.
d Calculate the mass of sodium chloride produced by this reaction.

4.2 Performing volumetric analyses – titrations

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- describe the equipment used in volumetric analysis and explain its use and measurement uncertainty
- perform stoichiometric calculations using the acid–base titration data.

Now that you know how to prepare a standard solution, you will learn how to perform a volumetric analysis. This technique is an experimental method using specialised glassware that is widely used to analyse solutions of acids and bases. You will use experimental data and stoichiometry to calculate the concentration of the acid or base being analysed.

TITRATION

Volumetric analysis involves reacting a measured volume of a standard solution with a measured volume of a second solution in a process called a **titration**. In a titration, a standard solution (with a known concentration of solute) is used to determine the unknown concentration of a solute in a second solution. The process involves gradually adding the standard solution to the unknown solution until the solutes in both solutions have fully reacted. This is called the **equivalence point**. The solutes must react in a predictable and measurable manner, as described by a balanced chemical equation. Using this information, calculations (like the Worked examples in the previous module) can be performed to determine the unknown concentration of a solute in the second solution.

> The point during a titration at which the reactants are present in equivalent amounts, as indicated by the coefficients in the balanced chemical equation for the reaction, is called the equivalence point.

The number of moles of solute in the standard solution can be calculated from its concentration and volume. By using the **mole ratio** from the equation for the reaction, the number of moles of the solute in the solution of unknown concentration can be determined. The unknown solution concentration can then be calculated from the number of moles and the volume of the solution.

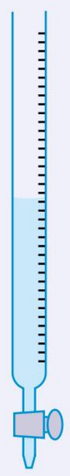
Once the concentration of a solution has been determined from a titration, the solution is said to be standardised.

EQUIPMENT USED IN VOLUMETRIC ANALYSIS

The laboratory equipment shown in Table 4.2.1 is used to make precise measurements of volumes. These instruments, combined with calculations similar to those in Module 4.1, can help scientists determine unknown concentrations of acids and bases.

For example, if you want to determine the concentration of a hydrochloric acid solution, you can react the hydrochloric acid with a standard solution of sodium carbonate. Precisely calibrated glassware is used to carry out the analysis.

TABLE 4.2.1 Laboratory equipment used to determine the concentration of a solution of hydrochloric acid by volumetric analysis

Equipment	Visual reference	Use
volumetric flask		A volumetric flask is used to prepare a standard solution of sodium carbonate. An accurately weighed sample of sodium carbonate is placed in the flask and dissolved in deionised water to form a specific volume of solution.
pipette		A **pipette** is used to accurately measure a specific volume of the solution of hydrochloric acid. This known volume, or **aliquot**, is then poured into a conical flask ready for analysis.
burette		A **burette** delivers a **titre** of the sodium carbonate standard solution. A titre is an accurately known volume of solution measured by the burette during a titration.

The reaction between hydrochloric acid and sodium carbonate solution is represented by the equation:

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

Using the equipment shown in Figure 4.2.1, the solution of sodium carbonate is slowly added (titrated) from the burette to the acid solution in the conical flask until the equivalence point is reached. Because these reactants are in a 1:2 ratio, the equivalence point occurs when the number of moles of Na_2CO_3 added from the burette is exactly half the number of moles of HCl present in the conical flask.

The reaction is complete when the equivalence point is reached. The concentration and volume of sodium carbonate (from the burette) required are now known, as is the volume of the aliquot of hydrochloric acid used. The concentration of the acid can now be calculated.

As both acid and base solutions are often colourless, an acid–base indicator is added to determine when the reaction is complete. The indicator chosen should change colour as close to the equivalence point as possible. The **end point** is the point during the titration at which the indicator changes colour. For an accurate analysis, the end point should be very close to the equivalence point. The key to a successful titration is using an appropriate acid–base indicator. You will learn about acid–base indicators in Module 4.3.

The end point of a titration occurs when the indicator changes colour.

Figure 4.2.1 shows how the equipment listed would be used to complete the titration for the reaction between sodium hydroxide (NaOH) and hydrochloric acid (HCl).

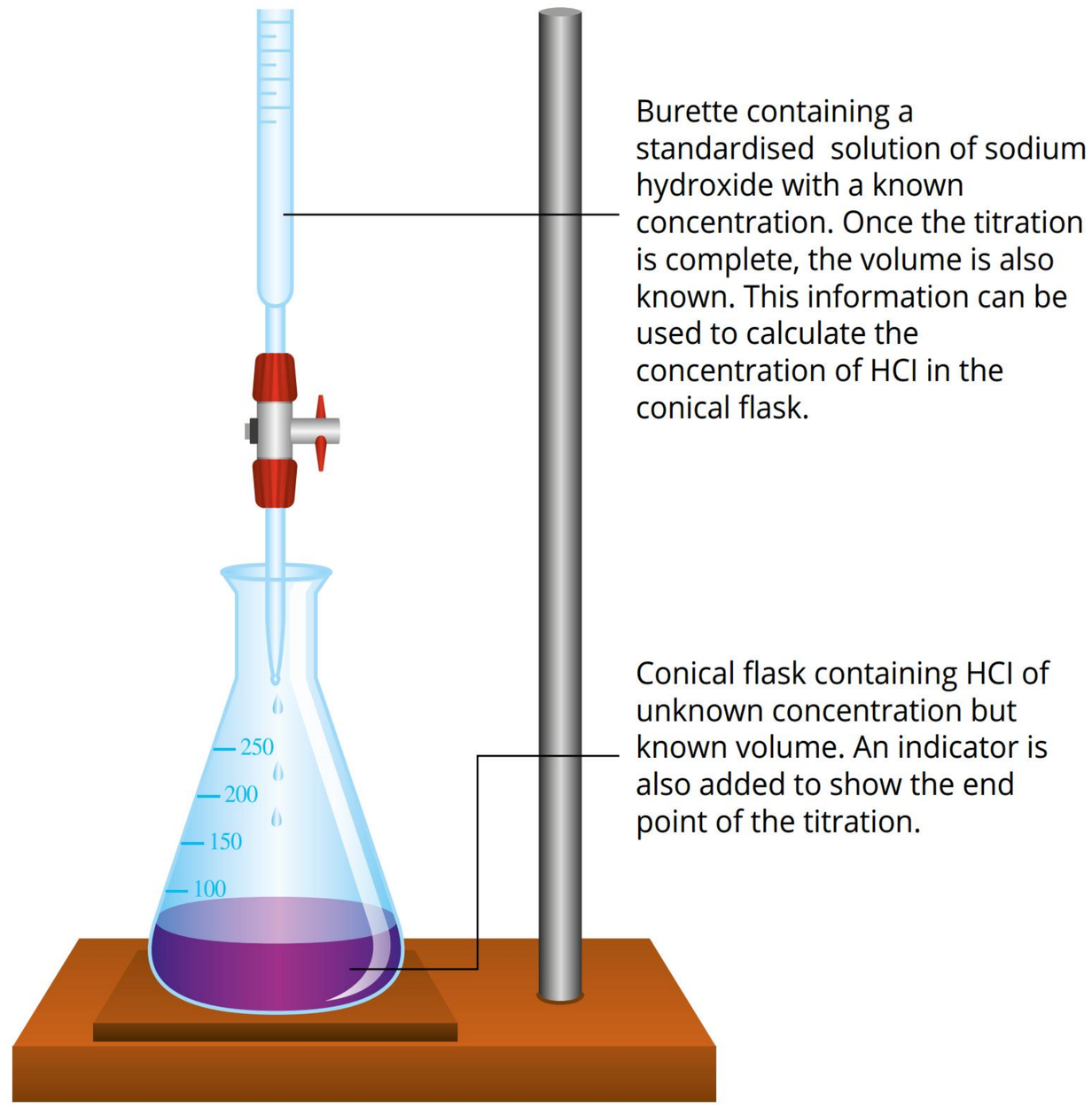


FIGURE 4.2.1 The equipment used in the titration of NaOH (in the burette) to determine the concentration of HCl (in the conical flask)

As outlined above, the steps involved in an acid–base titration are as follows:

1 A known volume, or aliquot, of one of the solutions is measured using a pipette and transferred into a conical flask, as shown in Figure 4.2.2.
2 The other solution is added to the burette, and the volume in the burette is recorded.
3 A few drops of an appropriate acid–base indicator are added to the solution in the conical flask, so that a colour change signals the point at which the titration should stop.
4 The solution from the burette is dispensed slowly into the conical flask until the indicator changes colour permanently (Figure 4.2.3). This is the end point.

FIGURE 4.2.3 Titration from the burette into the conical flask containing the aliquot of the first solution

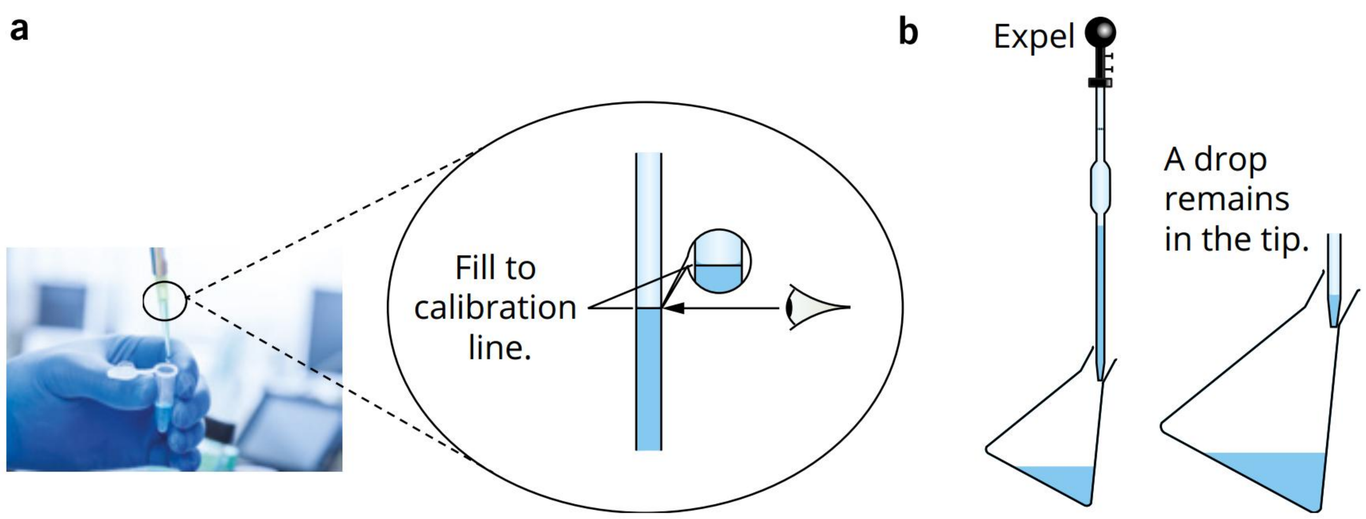


FIGURE 4.2.2 Taking an aliquot of a solution using a pipette. (a) Fill the pipette with the solution so that the bottom of the meniscus (curved upper surface of the solution) is level with the calibration line. (b) Expel the solution; the pipette has been designed so that a drop remains in the tip after an aliquot has been delivered.

Reading a burette scale

Burettes are usually calibrated in intervals of 0.10 mL. The volume of solution in a burette is measured at the bottom of the meniscus. The reading is estimated to be half the smallest division, 0.05 mL, as shown in Figure 4.2.4. The volume measurement in the burette shown is 22.20 mL.

The titre delivered from the burette is calculated by subtracting the initial burette reading from the final burette reading. To minimise errors, the titration is repeated several times, and the **average titre** is found. Usually, three **concordant titres** are used to find this average. Concordant titres are titres that are within a range of 0.10 mL from highest to lowest of each other.

The volume of one single drop from a burette is about 0.05 mL, so taking the average of three results assumes that the results will be no more than one drop over or one drop under the accurate titre.

Consider the titration data represented in Table 4.2.2.

FIGURE 4.2.4 The burette is read from the bottom of the meniscus, and the volume is estimated to the second decimal place.

TABLE 4.2.2 Titration data collected over five trials

Titration number	1	2	3	4	5
Final burette reading	20.20	40.85	20.65	41.85	21.85
Initial burette reading	0.05	21.00	1.05	22.05	2.00
Titre (mL)	20.15	19.85	19.60	19.80	19.85

The first reading is a rough reading that gives an idea of the approximate end point. Titres 2, 4 and 5 are the concordant titres: they are within 0.10 mL from highest to lowest of each other. The difference between the highest and lowest readings is 19.85 – 19.80 = 0.05 mL, which is within the acceptable range for concordant results. The average (mean) titre is:

$$\frac{19.85 + 19.80 + 19.85}{3} = 19.83\,\text{mL}$$

Concordant titres are titres that are within a range of 0.10 mL from highest to lowest of each other.

Rinsing volumetric glassware

To ensure that glassware is completely clean, it is rinsed before a titration is conducted. This removes any trace chemicals from the glassware and makes the analytical results more precise and accurate. Table 4.2.3 describes the correct rinsing process for the glassware used in titrations. Rinsing with the wrong liquid or solution can cause errors in the analysis.

TABLE 4.2.3 Rinsing glassware for volumetric analysis

Glassware	Correct	Incorrect
burette pipette	The final rinse of a burette or pipette should be with the acid or base they are about to be filled with.	Rinsing with water will dilute the acid or base solution.
volumetric flask titration flask (conical flask)	Volumetric and titration flasks should only be rinsed with deionised water.	Rinsing with acidic or basic solutions will introduce unmeasured amounts of acids or bases into the flask that can react and affect results.

CALCULATIONS IN VOLUMETRIC ANALYSIS

In this section, you will learn how to calculate the concentration of the acid or base being analysed using data from a titration.

Consider the data gained in an acid–base titration in which the concentration of a dilute solution of hydrochloric acid was determined by titration with a standard solution of sodium hydroxide.

The data gained from the titration are summarised in Table 4.2.4.

TABLE 4.2.4 Sample data obtained from a volumetric analysis

Volume of aliquot of HCl	25.00 mL
Concentration of standard NaOH solution	1.00 mol L^{-1}
Titre volumes of NaOH	25.05 mL, 22.10 mL, 22.00 mL, 22.05 mL

The concentration of hydrochloric acid is calculated by following a number of steps. These steps are summarised in the flow chart shown in Figure 4.2.5.

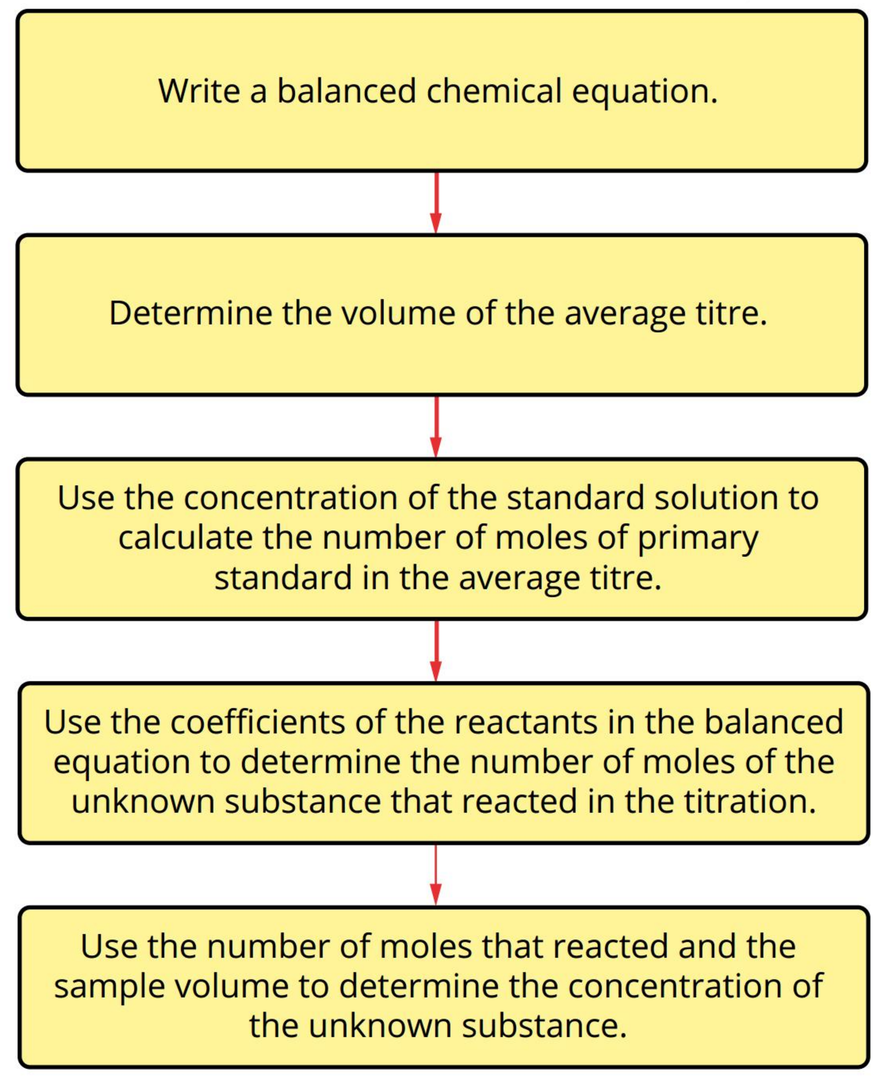


FIGURE 4.2.5 This flow chart summarises the steps in the calculation of the concentration of an unknown substance using the data from a titration in which the standard solution was in the burette.

Worked example 4.2.1 shows how the concentration of an acid can be determined using data from an acid–base titration.

Worked example 4.2.1

SIMPLE TITRATION CALCULATION

The concentration of a hydrochloric acid (HCl) solution was determined by titration with a standard solution of sodium hydroxide (NaOH).

A 25.00 mL aliquot of HCl was titrated with a 1.00 mol L^{-1} solution of NaOH. Titres of 25.05 mL, 22.10 mL, 22.05 mL and 22.00 mL were required to reach the end point.

Calculate the concentration of the hydrochloric acid solution.

Thinking	Working
Write a balanced chemical equation for the reaction.	An acid is reacting with a metal hydroxide, or base, so the products will be a salt and water: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

Determine the average volume of the concordant titres.	The titre of 25.05 mL is discarded because it is not concordant (i.e. it is not within a range of 0.10 mL from highest to lowest of the other titre volumes). $\text{average titre} = \frac{22.10 + 22.05 + 22.00}{3}$ $= 22.05\ \text{mL}$
Calculate the number of moles of the standard solution that was required to reach the end point.	$n(\text{NaOH}) = cV$ $= 1.00 \times 0.022\,05$ $= 0.022\,05\ \text{mol}$
Use the reactant coefficients in the balanced equation to calculate the number of moles of the unknown substance that would have reacted with the given number of moles of the standard solution.	$\text{mole ratio} = \frac{n(\text{HCl})}{n(\text{NaOH})} = \frac{1}{1}$ $n(\text{HCl}) = n(\text{NaOH})$ $= 0.022\,05\ \text{mol}$
Determine the concentration of the unknown substance.	$c(\text{HCl}) = \frac{n}{V}$ $= \frac{0.022\,05}{0.025\,00}$ $= 0.882\ \text{mol L}^{-1}$
Express your answer to the appropriate number of significant figures.	The final result is rounded to 3 significant figures corresponding to the smallest number of significant figures in the original data. Four significant figures are used in the earlier steps of the calculation to avoid rounding off errors. Concentration of HCl = $0.882\ \text{mol L}^{-1}$

➤ Try yourself 4.2.1

SIMPLE TITRATION CALCULATION

The concentration of a barium hydroxide ($Ba(OH)_2$), solution was determined by titration with a standard solution of hydrochloric acid (HCl).

A 10.00 mL aliquot of $Ba(OH)_2$ solution was titrated with a $0.125\ \text{mol L}^{-1}$ solution of HCl. Titres of 17.25 mL, 17.30 mL, 17.40 mL and 17.20 mL of HCl were required to reach the end point.

Calculate the concentration of the barium hydroxide solution.

Titrations that involve dilution

It is often necessary to dilute a solution before carrying out a titration in order to obtain concentrations that are more convenient to use. This will result in titres that are within the volume range of the burette.

Suppose you want to perform an acid–base titration to find the concentration of hydrochloric acid in a concrete cleaner. The concrete cleaner is so concentrated that it has to be accurately diluted before the titration. The following additional data are recorded:

- the volume of the aliquot of undiluted concrete cleaner
- the volume of diluted solution that is prepared.

The data obtained from such a titration are summarised in Table 4.2.5.

TABLE 4.2.5 Data from a titration involving diluted concrete cleaner

Volume of undiluted concrete cleaner	25.00 mL
Volume of diluted concrete cleaner	250.0 mL
Volume of titre of diluted concrete cleaner	19.85 mL
Concentration of standard Na_2CO_3 solution	0.448 mol L^{-1}
Volume of aliquot of Na_2CO_3 solution	20.00 mL

In this titration, 25.00 mL of concrete cleaner was diluted to 250.0 mL in a volumetric flask prior to taking a sample for titration. This means the **dilution factor** is $\frac{250.0}{25.00} = 10.00$. The undiluted concrete cleaner will be 10.00 times more concentrated than the concentration of the aliquot. This will be taken into account in the calculations.

The steps required to calculate the concentration of undiluted concrete cleaner are summarised in the flow chart shown in Figure 4.2.6.

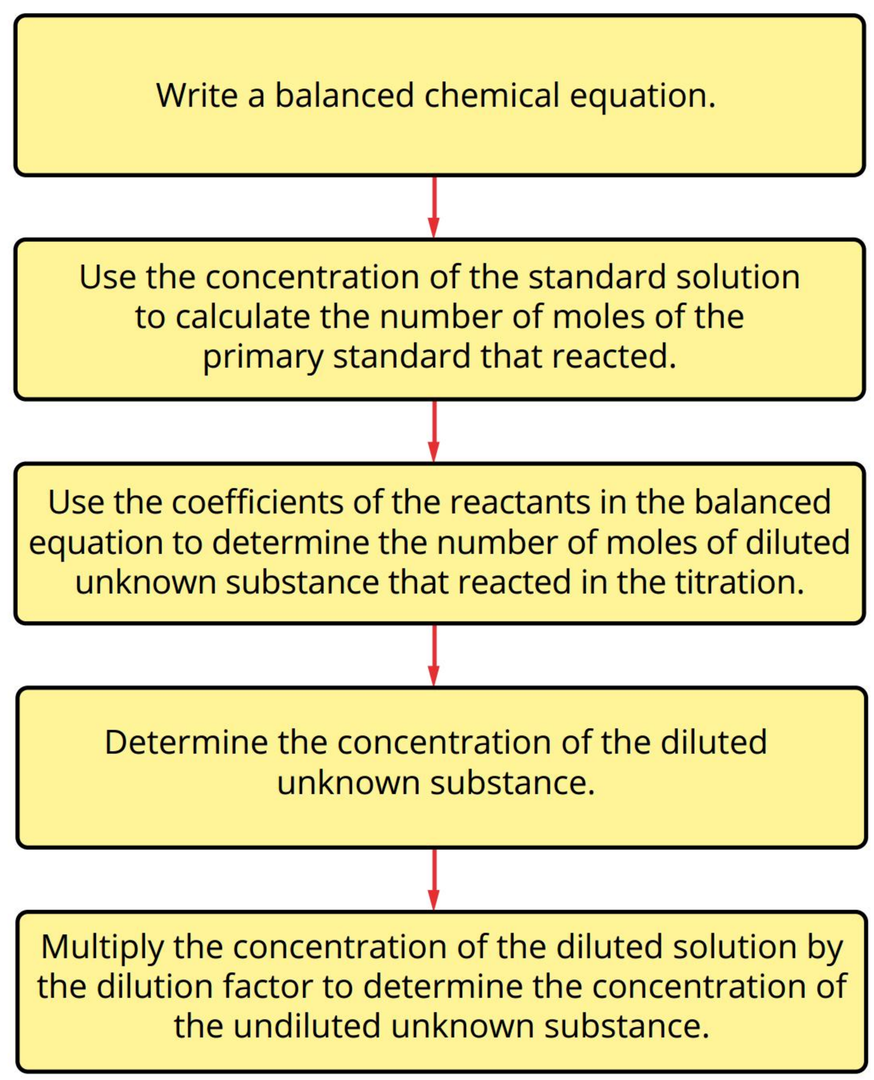


FIGURE 4.2.6 This flow chart shows the steps used in the calculation of the concentration of an unknown substance that has been diluted for use in a titration.

Worked example 4.2.2

A TITRATION CALCULATION THAT INVOLVES DILUTION

A commercial concrete cleaner contains hydrochloric acid (HCl). A 25.00 mL volume of cleaner was diluted to 250.0 mL in a volumetric flask.

A 20.00 mL aliquot of 0.448 mol L^{-1} sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added, and the solution was titrated with the diluted cleaner. The indicator changed colour permanently from yellow to pink when 19.85 mL of the cleaner was added.

Calculate the concentration, in mol L^{-1}, of hydrochloric acid in the concrete cleaner.

Thinking	Working
Write a balanced chemical equation.	A dilute acid is reacting with a metal carbonate, so the products will be a salt, water and carbon dioxide gas: $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$
Using the concentration of the standard solution, calculate the number of moles of the known substance that reacted in the titration. Remember that volume must be expressed in litres.	$n(Na_2CO_3) = cV$ $= 0.448 \times 0.02000$ $= 0.008960\,mol$
Use the reactant coefficients in the balanced equation to calculate the number of moles of the diluted unknown solution that reacted in the titration.	$\frac{n(HCl)}{n(Na_2CO_3)} = \frac{2}{1}$ $n(HCl) = \frac{2}{1} \times n(Na_2CO_3)$ $= \frac{2}{1} \times 0.008960$ $= 0.01792\,mol$
Calculate the concentration of the diluted unknown solution reacting in the titration.	$V(\text{diluted HCl}) = 0.01985\,L$ $c(HCl) = \frac{n}{V}$ $= \frac{0.01792}{0.01985}$ $= 0.9028\,mol\,L^{-1}$
Multiply by the dilution factor to determine the concentration of undiluted concrete cleaner. Express your answer to the appropriate number of significant figures.	$\text{Dilution factor} = \frac{250.0}{25.00} = 10.00$ So, undiluted $c(HCl)$ = diluted $c(HCl) \times 10.00$ $= 0.9028 \times 10.00$ $= 9.028\,mol\,L^{-1}$ The final result is rounded to 3 significant figures corresponding to the smallest number of significant figures in the original data. Four significant figures are used in the earlier steps of the calculation to avoid rounding off errors. Concentration of HCl in the concrete cleaner is $9.03\,mol\,L^{-1}$

➤ Try yourself 4.2.2

A TITRATION CALCULATION THAT INVOLVES DILUTION

A commercial concrete cleaner contains hydrochloric acid (HCl). A 10.00 mL volume of cleaner was diluted to 250.0 mL in a volumetric flask.

A 20.00 mL aliquot of $0.241\,mol\,L^{-1}$ sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added, and the solution was titrated with the diluted cleaner. The indicator changed colour permanently from yellow to pink when 18.70 mL of the cleaner was added.

Calculate the concentration, in $mol\,L^{-1}$, of hydrochloric acid in the concrete cleaner.

Uncertainties

The accuracy with which the volumes of the aliquot and titre are measured in volumetric analysis depends on the calibration of the equipment used. Often, uncertainties are indicated on the equipment being used. However, if no **uncertainty** is indicated, the accepted uncertainty is always half the smallest division. For digital instruments, the absolute uncertainty is equal to the smallest decimal place displayed. Balance uncertainties depend on the number of decimal points. There are always errors associated with measurements of quantities such as mass and volume made during experimental work. These are some typical uncertainties associated with volumetric analysis:

- 20 mL pipette: ±0.03 mL
- 50 mL burette: ±0.05 mL for each reading
- 250 mL volumetric flask: ±0.3 mL
- 100 g capacity top-loading balance: ±0.001 g
- 60 g capacity analytical balance: ±0.0001 g.

Other graduated laboratory glassware provides less precise measures:

- 50 mL measuring cylinder: ±0.1 mL
- 50 mL graduated beaker: ±5 mL.

Precision and accuracy

Every measurement in a **quantitative analysis** is subject to some form of error. Therefore, a calculation that makes use of these measurements will produce a result in which the errors have accumulated.

If repeated measurements of the same quantity yield values that are in close agreement, then the measurement is said to be **precise**. For example, a titration is generally repeated until at least three titres are obtained that are within narrowly specified limits. These are called concordant titres. Repeated measurement of the titres increases the precision of the result and minimises errors that may have affected one titre more than others.

If the average of a set of measurements of a quantity is very close to the true or accepted value of the quantity, then the measurement is said to be **accurate**. Figure 4.2.7 compares accuracy and precision.

Accuracy is the ability to obtain the correct measurement. To obtain accurate results, you must minimise systematic errors.

Precision is the ability to consistently obtain the same measurement. To obtain precise results, you must minimise random errors.

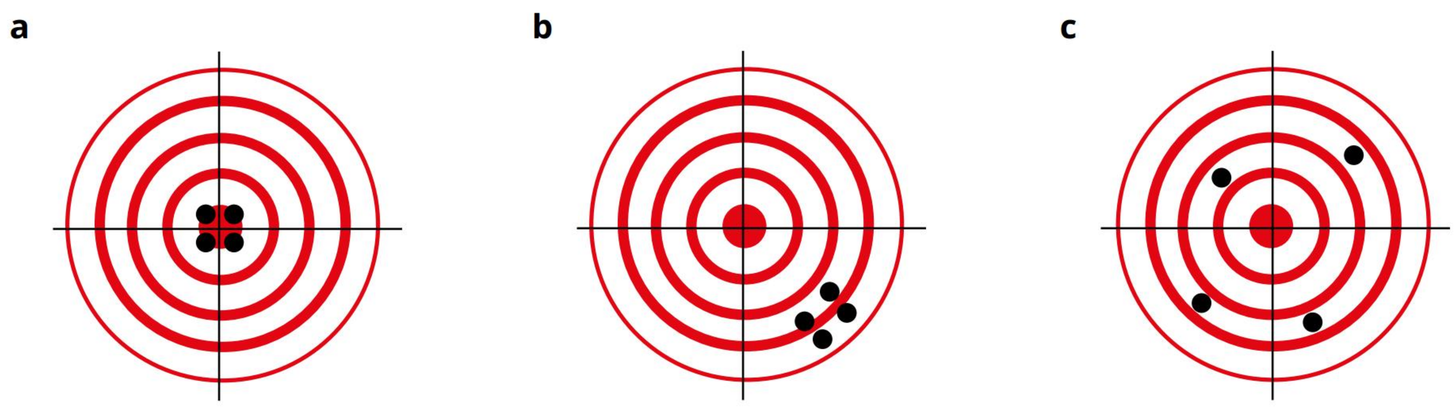


FIGURE 4.2.7 The holes in the targets illustrate the difference between accuracy and precision. Target (a) shows good accuracy and good precision. Target (b) illustrates poor accuracy but good precision, and target (c) shows both poor accuracy and poor precision. Analytical chemists aim to produce results that are both precise and accurate.

You can see that it is possible for a result to be precise but inaccurate.

Methods used for accurate quantitative analysis should be designed to minimise errors. Where errors cannot be avoided, any discussion of results should refer to the level of inaccuracy that may have accumulated. This requires an understanding of the different types of errors.

Types of errors

Mistakes

Mistakes are avoidable errors. Mistakes made during acid–base titrations could include:

- misreading the numbers on a scale
- mistakenly using a pipette of incorrect volume
- spilling a portion of a sample
- incorrect rinsing of glassware.

A measurement that involves a mistake must be rejected and not included in any calculations or averaged with other measurements of the same quantity. Mistakes are not generally referred to as errors.

Systematic errors

A **systematic error** produces a constant bias in a measurement that cannot be eliminated by repeating the measurement. Systematic errors that affect an acid–base titration could include:

- a faulty balance
- a 20.0 mL pipette that delivers 20.2 mL
- an unsuitable indicator being used
- the presence of extra components in the sample, other than the chemical being analysed, that react during the titration.

Whatever the cause, the resulting error is in the same direction for every measurement and the average will be either higher or lower than the true value.

Systematic errors are eliminated or minimised through the calibration of apparatus and the careful design of a procedure. If the error cannot be eliminated, an effort should be made to determine its size so that the error can be taken into account in calculations.

Random errors

Random errors follow no regular pattern. The measurement is sometimes too large and sometimes too small. Random errors in volumetric analysis could include:

- inherent uncertainty in the last value after the decimal place in the measurement of the mass of a primary standard on an analytical balance
- difficulty in judging where the meniscus sits on the line when measuring a volume using a pipette
- difficulty in judging the fraction between two 0.1 mL scale markings on a burette.

The effects of random errors can be reduced by taking multiple measurements of the same quantity, then calculating an average. In volumetric analysis, the average of three concordant titres is used to reduce random error.

4.2 Review

SUMMARY

- Volumetric analysis is an analytical technique for determining the concentration of a solution by titrating it against a solution of known concentration (a standard solution) and volume.
- Volumetric flasks, pipettes and burettes are accurately calibrated pieces of glassware used in volumetric analysis.
- The point during a titration at which the reactants are present in equivalent amounts, as indicated by the coefficients in the equation for the reaction, is called the equivalence point.
- The end point is the point at which the indicator changes colour.
- The end point in an acid–base titration must be at or close to the equivalence point.
- Three concordant titres are usually obtained during volumetric analysis. Concordant titres lie within 0.10 mL from highest to lowest of each other.
- The concentration of acidic or basic solutions can be determined by volumetric analysis.
- When rinsing glassware before a titration, it is important to ensure that:
  - the conical and volumetric flasks are rinsed with deionised water
  - the burette and pipette are rinsed with the solution to be transferred by them.
- Dilution of the unknown solution is sometimes required to obtain manageable titre volumes.
- The mole ratio in a balanced chemical equation allows the number of moles of a species in the equation to be calculated from the number of moles of any other species.
- All quantitative measurements involve an error and have an uncertainty associated with them.
- Accuracy refers to how closely a measurement agrees with the true value.
- Precision refers to how closely a set of measurements are to each other.
- A systematic error produces a constant bias in a measurement, which cannot be eliminated by repeating the measurement.
- A random error has an equal chance of being greater or lower than the true value.

KEY QUESTIONS

Describe

1 A solution of sodium hydroxide (NaOH) was standardised by titrating it using 25.00 mL aliquots of a standard solution of potassium hydrogen phthalate. The concentration of ethanoic acid (CH_3COOH) in vinegar was then found by diluting a 10.00 mL aliquot of vinegar into a volumetric flask. 20.00 mL aliquots of the diluted vinegar were then taken from the volumetric flask and titrated with the standardised NaOH solution.

a Name the solution that would have been made directly from a primary standard.

b Identify the solution that should be used to rinse the following pieces of equipment.

i 10.00 mL pipette

ii volumetric flask used to dilute vinegar

iii burette

2 Identify which of the following would be concordant titres: 15.40 mL, 16.20 mL, 16.25 mL, 17.00 mL and 16.15 mL. Explain your decision.

3 Distinguish between the end point and the equivalence point of a titration.

Apply

4 Explain the use of each of the following pieces of equipment.

a burette

b pipette

c volumetric flask

Analyse

5 The following titres were obtained when a solution of sulfuric acid (H_2SO_4) was titrated against a standard solution of potassium hydroxide.

Trial	1	2	3	4	5
Titre (mL)	26.30	25.45	25.40	25.60	25.45

Calculate the average volume of H_2SO_4 that would be used in volumetric calculations.

6 A 20.00 mL aliquot of sulfuric acid solution is neutralised by the addition of 22.95 mL of 1.34 mol L^{-1} potassium hydroxide solution. The equation for the reaction is:

$$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

Calculate the concentration of the sulfuric acid solution.

7 The concentration of ethanoic acid (CH_3COOH) in vinegar was determined by titration with a standardised solution of sodium hydroxide (NaOH). A 25.00 mL aliquot of vinegar required 21.55 mL of 0.995 mol L^{-1} NaOH to reach the end point.

- **a** Write an equation for the reaction between ethanoic acid and sodium hydroxide.
- **b** Calculate the number of moles of NaOH used in the titration.
- **c** Calculate the number of moles of ethanoic acid that reacted.
- **d** Calculate the concentration of ethanoic acid in the vinegar.
- **e** During the titration, several pieces of glassware were used. State which liquid or solution should be used to rinse each of the pieces of glassware below, immediately before use.
  - **i** pipette
  - **ii** burette
  - **iii** conical flask

8 A commercial concrete cleaner contains hydrochloric acid. A 25.00 mL volume of cleaner was diluted to 250.0 mL in a volumetric flask. A 25.00 mL aliquot of 0.505 mol L^{-1} sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added, and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 23.95 mL of the diluted cleaner had been added.

The equation for the reaction is:

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + 2H_2O(l)$$

Determine the concentration of hydrochloric acid in the concrete cleaner.

9 A student standardised a solution of sodium hydroxide using a standard hydrochloric acid solution.

A 20.00 mL aliquot of the sodium hydroxide solution was titrated with a 0.0932 mol L^{-1} hydrochloric acid solution. The titres recorded were 18.65 mL, 18.85 mL, 18.90 mL and 18.95 mL.

- **a** Write a balanced equation for the reaction between sodium hydroxide and hydrochloric acid.
- **b** Calculate the average of the concordant titres of hydrochloric acid.
- **c** Calculate the concentration, in mol L^{-1}, of the sodium hydroxide solution.

10 In an analysis to determine the accurate concentration of ethanoic acid (CH_3COOH) in a sample of vinegar, a solution was titrated with a standardised sodium hydroxide solution. Aliquots of the vinegar were transferred to a conical flask using a 20.00 mL pipette and titrated against the sodium hydroxide in a burette. The calculated concentration was higher than the value given on the bottle label. Which one or more of the following errors would account for the higher than expected calculated concentration? Justify your answers.

- **a** The 20.00 mL pipette was rinsed only with deionised water prior to its use.
- **b** The burette was rinsed only with deionised water prior to its use.
- **c** The conical flask was rinsed with the vinegar solution prior to its use.

GO TO ➤ **Practical Investigation 1**

4.3 Acid–base indicators

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand why acid–base indicators have a different colour in acidic solutions to their colour in basic solutions
- explain the relationship between the pH range of an acid–base indicator and its pK_a value
- determine the appropriate indicator for a titration given the equivalence point for the reaction and pH range of the indicator.

The key to an acid–base titration is selecting an appropriate acid–base indicator to match the equivalence point of a reaction. **Acid–base indicators** are weak acids or weak bases that are different colours in acidic solutions and basic solutions. The conjugate acid form of the indicator is one colour, and the conjugate base form is another. Acid–base indicators are used to distinguish between acidic and basic solutions. Indicators can be used to determine the pH of a solution, and they are also used for acid–base analyses such as acid–base titrations. In this module, you will explore the range of acid–base indicators commonly used in laboratory titrations.

COMMON INDICATORS

One of the characteristic properties of acids and bases is their ability to change the colour of certain plant extracts. Litmus is a purple dye obtained from lichen. In the presence of acids, litmus turns red, and in the presence of bases, it turns blue. The colouring of rose petals, blackberries and red cabbage is also altered by acids and bases. Such plant extracts are called indicators.

Figure 4.3.1 shows the variation in colour that can be achieved using red cabbage as an indicator. As you can see, the colour of juice extracted from the leaves of red cabbage is dependent upon the pH of the solution.

Today, most indicators used in laboratories and industry, such as bromothymol blue, methyl orange and phenolphthalein, are commercially produced. Common indicators and their pH ranges can be seen in Figure 4.3.2. These indicators can be used to determine the pH of solutions over a small range of values only and are useful in acid–base analyses.

FIGURE 4.3.1 The colour of extract from red cabbage in solutions (from left to right) of pH 1, pH 3, pH 5, pH 8 and pH 10

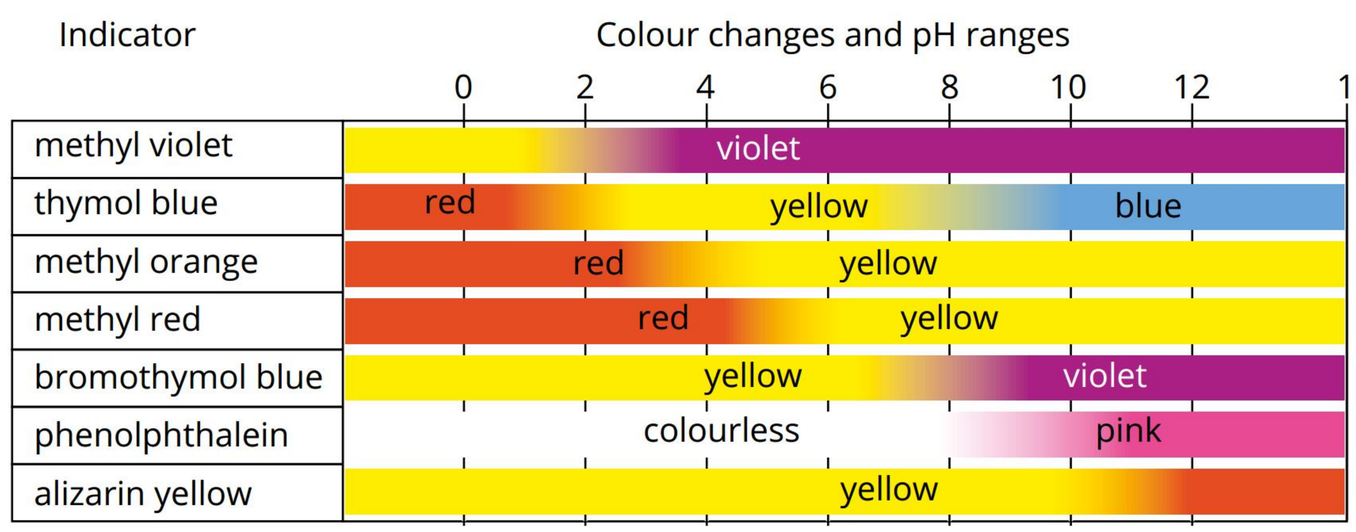


FIGURE 4.3.2 Common indicators and their pH ranges

> **An indicator is a weak acid or weak base where the conjugate acid/base pair has different colours.**

pH RANGE OF AN INDICATOR

Indicators are large organic molecules whose colour changes in response to changes in the pH of the solution they are dissolved in. They are either weak acids or weak bases. The notation HIn is used as a general form for an indicator, recognising that it is a complex organic molecule with acidic properties.

In solution, the acid form of the indicator is in equilibrium with its conjugate base, as shown in the following equation:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

The position of equilibrium changes depending on the pH. The colour of the acid form of an indicator, HIn, and the colour of its conjugate base, In^-, are different. The acid or base colour of an indicator is visible at low indicator concentrations.

The dissociation constant for the acid–base indicator ionisation is:

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

The indicator changes colour when the concentration of the acid, HIn, is equal to the concentration of its conjugate base, In^-. That is, the colour change will occur when $H_3O^+ = K_a$. This means that the colour change occurs when the pK_a is equal to the pH.

For example, methyl orange is an indicator with a pK_a value of 3.7. It changes colour over a pH range of 3.2–4.4. Methyl orange and other common indicators will be discussed in the following sections.

According to the Brønsted–Lowry model of acids and bases, an acid and its conjugate base differ by the presence of a proton (H^+).

Universal indicator

Universal indicator is widely used to estimate the pH of a solution. It is a mixture of several indicators and changes through a range of colours from red to yellow, green, blue and violet. This can be seen in Figure 4.3.3. If a more accurate measurement of pH is needed, you can use a pH meter instead of universal indicator.

FIGURE 4.3.3 Universal indicator pH scale. When the universal indicator is added to a solution, it changes colour depending on the solution's pH. The tubes contain solutions of pH 1 to 12 from right to left. The light green tube (centre) is neutral, pH 7.

Bromothymol blue

Bromothymol blue is a widely used indicator. The indicator is yellow in acidic solutions and blue in basic solutions. In a neutral solution of pH 7.0, the colour of the indicator is green, midway between yellow and blue.

A chart showing the variation in colour of bromothymol blue from pH 0 to pH 14 is shown in Figure 4.3.4.

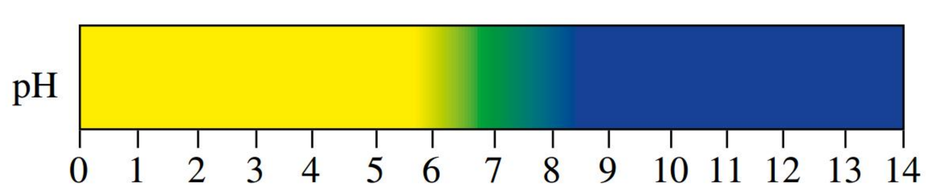


FIGURE 4.3.4 Bromothymol blue is yellow in acidic solutions and blue in basic solutions. The indicator changes colour over the pH range 6.0–7.6.

The equilibrium principles studied in Chapter 2 also apply to indicators. Le Châtelier's principle can be used to explain why indicators have different colours in acidic and basic solutions.

The equation for the ionisation of bromothymol blue in water is shown here. Bromothymol blue is a complex organic compound. For the sake of simplicity, the acid form of bromothymol blue can be represented as HBB and the base form as BB^-.

$$\underset{\text{yellow}}{HBB(aq)} + H_2O(l) \rightleftharpoons \underset{\text{blue}}{BB^-(aq)} + H_3O^+(aq)$$

The indicator colour you see depends upon the relative concentrations of HBB and BB^-.

When a few drops of bromothymol blue indicator are added to HCl solution, the additional H_3O^+ ions from HCl shift the indicator equilibrium system to the left:

$$\underset{\text{yellow}}{HBB(aq)} + H_2O(l) \rightleftharpoons \underset{\text{blue}}{BB^-(aq)} + H_3O^+(aq)$$

The concentration of HBB molecules is now much greater than the concentration of BB^- ions, and the solution has a yellow colour.

When the indicator is added to a solution of a base, the OH^- ions react with the HBB:

$$\underset{\text{yellow}}{HBB(aq)} + OH^-(aq) \rightleftharpoons \underset{\text{blue}}{BB^-(aq)} + H_2O(l)$$

The concentration of BB^- ions is now much greater than the concentration of HBB molecules, and the solution has a blue colour, as shown in Figure 4.3.5.

FIGURE 4.3.5 Bromothymol blue is yellow in acidic solutions (left), blue in basic solutions (right) and green in neutral solutions (centre).

At a pH of 7.0, the concentration of HBB molecules and the concentration of BB^- ions are equal. This is referred to as the transition point of bromothymol blue. At this point, the solution appears green, a mixture of blue and yellow.

Methyl orange

Methyl orange is a synthetic indicator often used in the analysis of weak bases. It is also used as a textile dye.

Methyl orange is red in acidic solutions and yellow in basic solutions. The indicator changes colour between pH 3.1 and pH 4.4. Between these pH values, the indicator has an orange colour.

A colour chart for methyl orange indicator is shown in Figure 4.3.6.

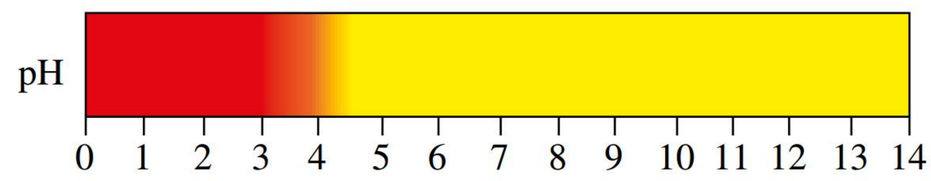


FIGURE 4.3.6 Methyl orange is red in acidic solutions and yellow in basic solutions. The indicator changes colour over the pH range 3.1–4.4.

Methyl orange is a weak acid. The acidic and basic forms of the indicator are in equilibrium in solution. Their structures are shown in Figure 4.3.7

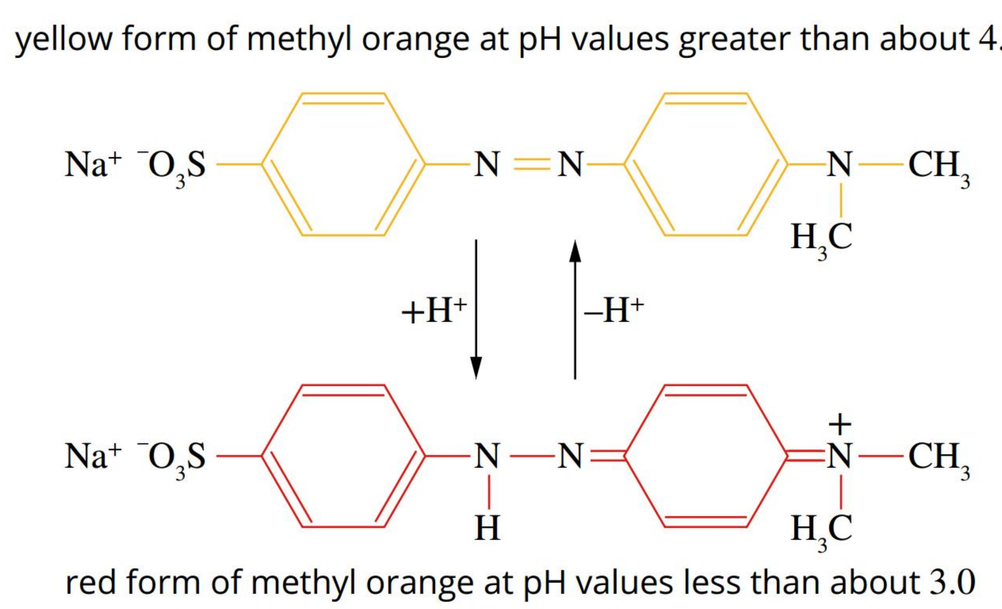


FIGURE 4.3.7 The structure of methyl orange is dependent upon the pH of the solution. The red form of methyl orange has a different structure from the yellow form.

Phenolphthalein

Phenolphthalein is a synthetic indicator used in the analysis of weak acids. In the past, it was also used as the active ingredient in some laxatives.

In acidic solutions, phenolphthalein is colourless, whereas in basic solutions, it has a pink to magenta colour. Phenolphthalein changes colour over the pH range 8.3–10.0.

A colour chart for phenolphthalein indicator is shown in Figure 4.3.8.

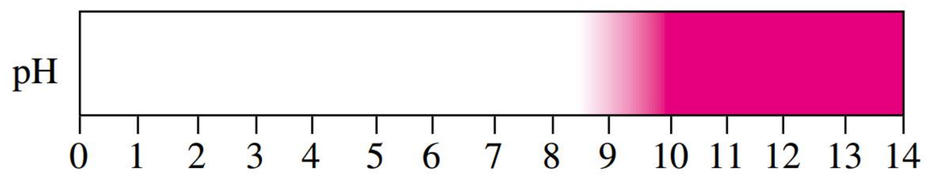


FIGURE 4.3.8 Phenolphthalein is colourless in solutions when the pH is below 8.3 and pink when the pH is greater than 10. The indicator changes colour over the pH range 8.3–10.0.

As you have seen, the colour of an indicator in acidic solution is distinctly different from its appearance in basic solution. Each indicator changes colour at a different pH. Indicators do not change colour at exactly pH 7.0, nor do they all change colour at the same pH. The pH of the colour transition depends upon the K_a of the indicator. Bromothymol blue changes colour between pH 6.0 and pH 7.6, methyl orange changes colour between pH 3.1 and pH 4.4, and phenolphthalein changes colour between pH 8.3 and pH 10.0. The range of pH values over which an indicator changes colour is known as the **indicator range**.

The colours of common acid–base indicators and the pH range over which they change colour were shown in Figure 4.3.2 on page 112. Table 4.3.1 summarises common indicators and their pH ranges.

TABLE 4.3.1 pH ranges of some common indicators

Indicator	pK_a	pH range of colour change	Colour change (acidic to basic)
methyl orange	3.7	3.1–4.4	red to yellow
bromophenol blue	4.2	3.0–4.6	yellow to blue
bromocresol green	4.7	3.8–5.4	yellow to blue
methyl red	5.1	4.4–6.2	pink to yellow
bromothymol blue	7.0	6.0–7.6	yellow to blue
phenol red	7.9	6.8–8.4	yellow to red
phenolphthalein	9.6	8.3–10.0	colourless to pink

USING INDICATORS IN VOLUMETRIC ANALYSIS

Indicators are particularly useful in determining the equivalence point of a **neutralisation reaction** between an acid and a base. Recall from Module 4.2 that the equivalence point is the point during a neutralisation reaction when the amount of acid and base are in stoichiometric ratios represented by the reaction equation. The end point is when the indicator changes colour. For an accurate volumetric analysis, the end point corresponds closely with the equivalence point.

A neutralisation reaction occurs when an acid reacts with a base to form a salt and water.

For example, hydrochloric acid and sodium hydroxide react according to the following equation:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

The equivalence point during this reaction is when the number of moles of HCl is equal to the number of moles of NaOH in the 1:1 ratio given by the equation.

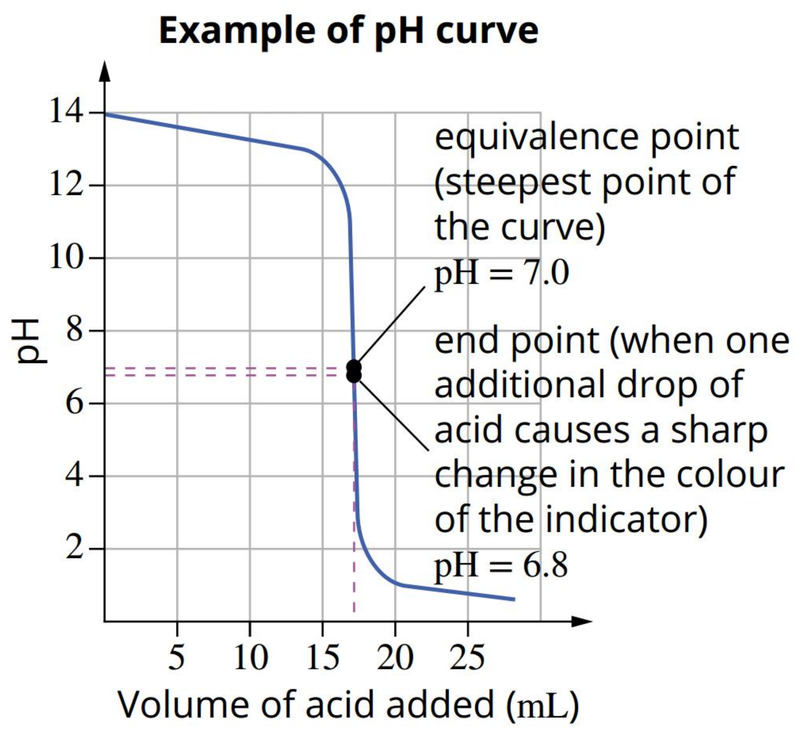


FIGURE 4.3.9 Titration curve for a strong acid being added to a strong base

The change in pH when a strong acid, such as HCl, is titrated against a strong base, such as NaOH, can be represented on a graph called a **titration curve** or **pH curve**. The equivalence point occurs when the gradient of the pH curve is steepest. An example of a pH curve is shown in Figure 4.3.9.

Near the equivalence point, the addition of a very small volume of HCl produces a large change in pH. In this titration, the pH changes from 10.0 to 4.0 with just one drop of acid! By using an indicator that changes colour within this pH range, such as bromothymol blue (which changes colour between pH 6.0 and pH 7.6), one drop will cause a colour change. This is referred to as a sharp end point. Therefore, knowing the pH range of an indicator is an important tool to ensure a sharp end point. Other indicators, including phenolphthalein (pH range 8.3–10.0), could also be used for this titration because they would also produce a sharp end point. In Module 4.4, you will learn how to interpret titration curves to identify the equivalence point of a titration.

Determining the transition point and pH range of an indicator

Remember from earlier in this module that indicators are weak Brønsted–Lowry acids.

The expression for the acidity constant of an indicator is:

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]}$$

The pH at which the indicator changes colour depends upon the value of the indicator's acidity constant, K_a. At the midpoint of the indicator colour change, the **transition point**, the concentrations of the acidic and basic forms of the indicator are equal, i.e. $[HIn] = [In^-]$.

At the transition point, the equilibrium expression simplifies to:

$$[H_3O^+] = K_a$$

The pH at the transition point can be calculated using $pH = -\log_{10}[H_3O^+]$. As a rule of thumb, the indicator range is one pH unit either side of the pH at the transition point.

For example, phenol red indicator (Figure 4.3.10) has a K_a of 10^{-8}. The concentration of hydrogen ions at the transition point is $10^{-8}\,mol\,L^{-1}$ and the pH is 8. The pH range of this indicator is approximately 8 ± 1, i.e. between pH 7.0 and pH 9.0.

> An indicator changes colour when the pH is equal to the value of the pK_a for the indicator.
>
> The pH range of an indicator is $pK_a \pm 1$.

FIGURE 4.3.10 Phenol red indicator at pH 5, pH 8 and pH 11 (from left to right)

4.3 Review

SUMMARY

- The colour of an indicator in acidic solution is distinctly different from its appearance in basic solution.
- Indicators are solutions of a weak acid or weak base in solution with its conjugate base or conjugate acid.
- The pH range of an indicator is related to the dissociation constant of the acid–base indicator ionisation reaction.
- The point in a titration at which the reactants have reacted in their correct mole ratios is called the equivalence point.
- A pH curve is a graph that plots pH against volume of titrant and is used to determine the equivalence point for a titration.
- The end point is the point during the titration at which the indicator changes colour.
- Indicators used in titrations must have a sharp end point.
- An indicator changes colour when the pH is equal to the value of the pK_a for the indicator.
- The pH range of an indicator is ± 1 pH unit of the pK_a value.
- The midpoint of the indicator colour change is referred to as the transition point.
- At the transition point, the concentrations of the acidic and basic forms of the indicator are equal, i.e. $[HIn] = [In^-]$.

KEY QUESTIONS

Describe

1 Refer to Table 4.3.1 on page 115 to determine what colour the following indicators will produce in pure water.

a methyl orange
b phenolphthalein
c bromothymol blue

2 Which indicator in Table 4.3.1 on page 115 would be best for distinguishing between a solution of pH 5 and a solution of pH 8?

3 Write the general equation for the equilibrium that exists between a weak acidic indicator and its conjugate base.

4 Explain the importance of selecting an indicator with an end point close to the equivalence point for the reaction.

Apply

5 Explain why universal indicator changes colour several times across a range of pH values.

6 Bromothymol blue is added to a solution of pH 5.

a Use Table 4.3.1 on page 115 to determine the colour of the solution.
b Explain what this indicates about the position of the equilibrium of the indicator reaction.

7 Determine the pH at which phenolphthalein would provide a sharp end point during a titration and what colour you would expect to see at the end point of a titration.

8 Use Le Châtelier's principle to explain how indicators change colour in acidic and basic solutions.

Analyse

9 Congo red is an acid–base indicator. The acid colour of the indicator is blue, and the base colour is red. The acid form of the Congo red molecule can be written as HCgr.

At pH 4 (the transition point), the concentration of HCgr is the same as the concentration of its conjugate base, Cgr^-.

a Represent the ionisation of Congo red in aqueous solution by completing the following equation.

$HCgr(aq) + H_2O(l) \rightleftharpoons$ _____ + _____

b Determine the colour of the solution at the following pH values.

i pH 4
ii neutral solution
iii pH 2
iv pH 12

4.4 Titration curves—analysis and interpretation

In Module 4.2, you were introduced to volumetric analysis, an analytical technique used by chemists to accurately determine the concentration of solutes in a solution. During a volumetric analysis, or titration, a measured volume of a standard solution is mixed with a measured volume of a solution in which the concentration of solute is unknown. The solutions are combined until the equivalence point is reached. This occurs when the reactants have just reacted completely in the mole ratio indicated by the coefficients in the balanced chemical equation. In an acid–base titration, an indicator is added to determine when the reaction is complete. Recall that the end point is the point during the titration at which the indicator changes colour. The indicator for each titration is selected so that the end point occurs as close as possible to the equivalence point. The choice of the indicator therefore requires a knowledge of the pH at the equivalence point of the titration.

TITRATION CURVES

During a titration, the pH of the solution in the conical flask changes as the solution is delivered from the burette. A graph showing pH against volume of titrant added is called a titration curve or pH curve. The change in pH when a strong acid, such as HCl, is titrated against a strong base, such as NaOH, is represented by the titration curves shown in Figure 4.4.1.

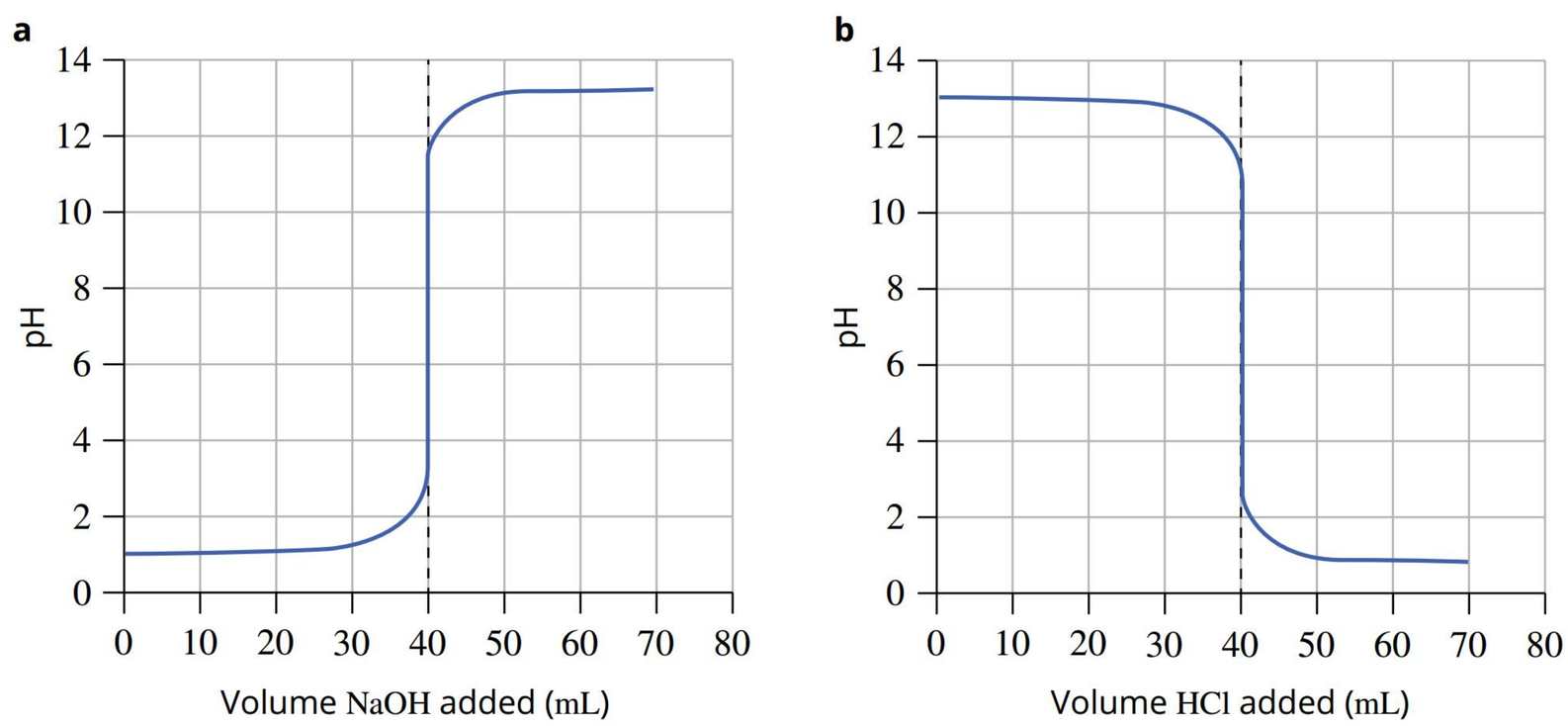


FIGURE 4.4.1 The titration curve for (a) the addition of a strong base to an aliquot of strong acid, and (b) the addition of a strong acid to an aliquot of a strong base.

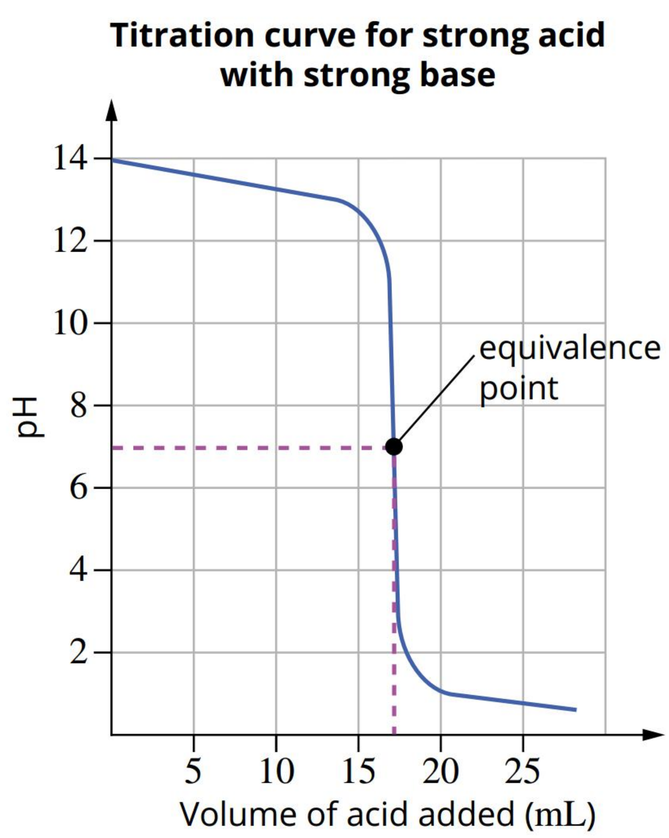


FIGURE 4.4.2 The titration curve for a strong acid (hydrochloric acid) being added to a strong base (sodium hydroxide)

The shape of a titration curve depends upon the combination of strong and weak acids and bases used in the titration. The equivalence point for a titration occurs when the gradient of the titration curve is steepest.

Consider the reaction between hydrochloric acid (HCl), a strong acid, and sodium hydroxide (NaOH), a strong base. The reaction between hydrochloric acid and sodium hydroxide is represented by the equation:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

The equivalence point during this reaction is when the number of moles of HCl is equal to the number of moles of NaOH in the 1:1 ratio given by the reactant coefficients in the equation. An example of a titration curve for this reaction is shown in Figure 4.4.2.

The initial pH of the NaOH solution is approximately 14. As HCl is added from the burette, the pH decreases slowly at first. Near the equivalence point, the addition of a very small volume of HCl produces a large change in pH. In this titration the pH changes from 10 to 4 with just one drop of acid!

By using an indicator that changes colour within this pH range, such as bromothymol blue which changes colour between pH 6.0 and 7.6, one drop of hydrochloric acid will cause a colour change. This is referred to as a **sharp end point**. Therefore, knowing the pH range of an indicator is an important tool to ensuring a sharp end point. Other indicators, including phenolphthalein (pH range 8.3 to 10.0), could be used for this titration because they would also produce a sharp end point for this reaction. (Indicator pH ranges were discussed in Module 4.3.)

The volume of acid added at the end point is very close to the equivalence point - the amount needed to stoichiometrically react according to the balanced equation. It is the volume of titre at the *end point* (when the colour change occurs) that is recorded for the titration.

Beyond the equivalence point, as more HCl is added, the pH decreases slowly again.

For more accurate volumetric analyses, a pH meter attached to a data logger can be used instead of an indicator. Data from the meter are used to plot a pH curve, and the equivalence point can be identified from the steepest section of the curve. Figure 4.4.3 shows a student using a digital pH meter to measure the pH of a solution as acid is added during a titration.

As small amounts of solution in the burette are progressively added to the titration flask, the student records the pH measurements and the corresponding burette reading.

The pH measurements shown in Table 4.4.1 were recorded during the titration of an ammonia solution (weak base) with a standard solution of 0.10 mol L^{-1} hydrochloric acid (strong acid). You can see from the titration curve in Figure 4.4.4 that the titre of hydrochloric acid needed to reach the equivalence point was about 24.5 mL, and the equivalence point occurs at a pH of 5.

FIGURE 4.4.3 A student uses a pH meter during a titration.

TABLE 4.1.1 pH change during a titration

Volume of HCl added (mL)	pH of conical flask solution
0.0	11.76
5.0	10.06
10.0	9.88
15.0	9.50
20.0	9.01
21.0	8.87
22.0	8.71
23.0	8.41
24.0	7.60
25.0	2.20
30.0	1.35
35.0	1.16

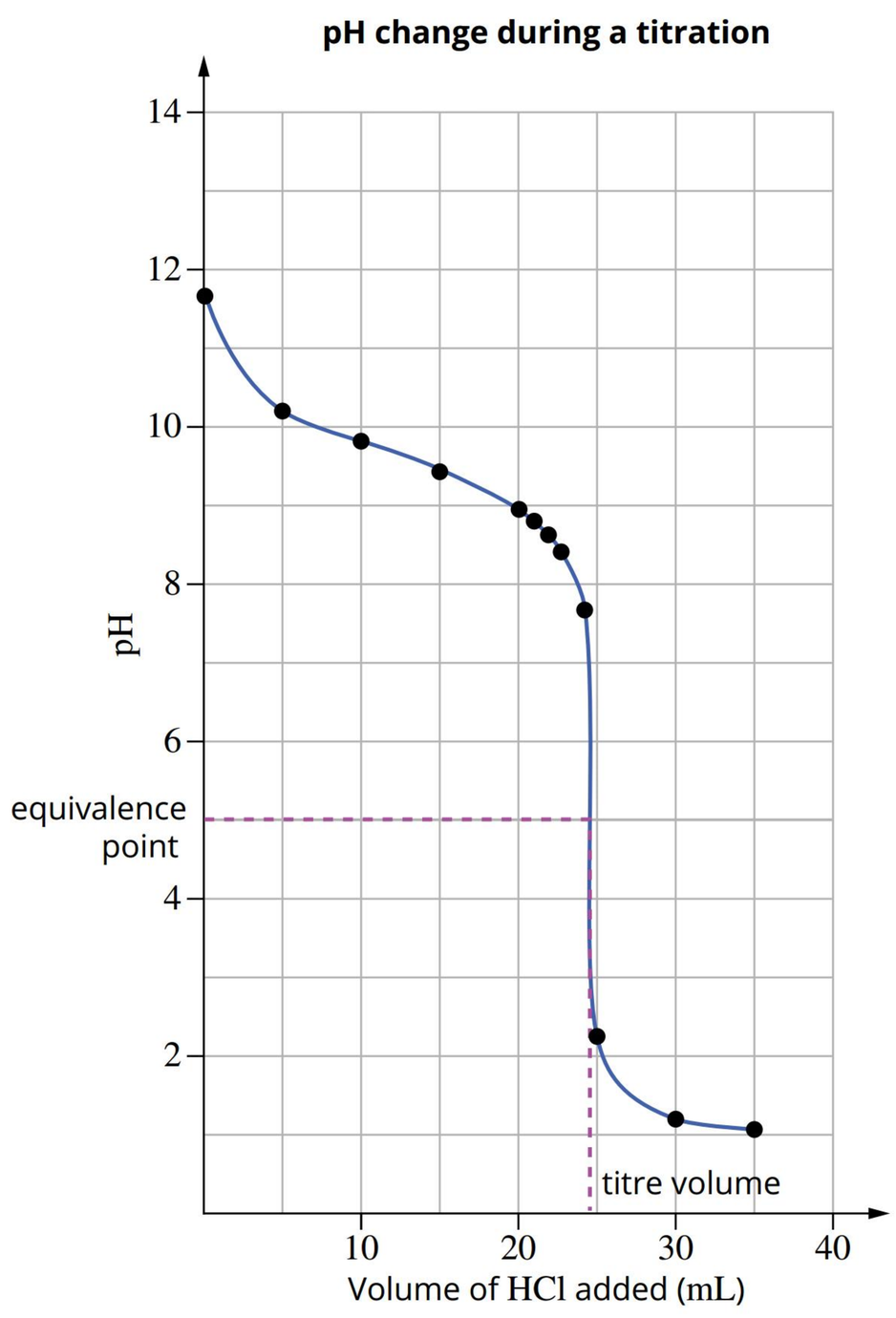


FIGURE 4.4.4 A titration curve showing how the pH of a solution of 0.1 mol L^{-1} NH_3(aq) changes as 0.1 mol L^{-1} HCl(aq) is added from a burette

pH meters need to be calibrated before use. Some pH probes linked to a computer can automatically store data into a spreadsheet and are able to simultaneously record pH and time elapsed. By adjusting the burette to a constant dripping rate (e.g. one drop per second) and reading data every 3 seconds for 5 minutes, a pH curve can be automatically generated and stored.

Indicators in volumetric analysis

You will remember from Module 4.3 that an indicator is in equilibrium with its conjugate base, represented by the following equation:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

The position of equilibrium changes depending on the pH. The colour of the acid form of an indicator, HIn, and the colour of its conjugate base, In^-, are different. The acid or base colour of an indicator is visible at low indicator concentrations.

The dissociation constant for the acid–base indicator ionisation is:

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

The indicator changes colour when the concentration of the acid, HIn, is equal to the concentration of its conjugate base, In^-. That is, the colour change will occur when $[H^+] = K_a$. This means that the colour change occurs when the pK_a is equal to the pH. For a basic indicator, the colour change occurs when the pK_b is equal to the pOH.

For example, methyl orange is an acidic indicator with a pK_a value of 3.7. It changes colour over a pH range of 3.1–4.4. Table 4.4.2 summarises some of the pH ranges of common acid–base indicators.

TABLE 4.4.2 The pH ranges of a number of common acid–base indicators

Indicator	pK_a	Colour of acid form	Colour of base form	pH range
methyl orange	3.7	red	yellow	3.1–4.4
bromothymol blue	7.0	yellow	blue	6.0–7.6
phenolphthalein	9.6	colourless	pink	8.3–10.0

When choosing an indicator for a titration, it is important to know the titration curve for the reaction.

Figure 4.4.5 compares the titration curves obtained when a strong acid is added to a strong base, and when a strong acid is added to a weak base. Note that there is a sharp drop in pH in both graphs at the equivalence point. However, because this drop occurs over different ranges, the choice of indicator is important in detecting the equivalence point. Phenolphthalein can be used successfully for the first titration but not for the second.

The equivalence point occurs when the gradient of the titration curve is steepest.

The end point occurs when the indicator changes colour.

Phenolphthalein, which changes colour in the pH range 8.3–10.0, gives a sharp end point in Figure 4.4.5a but a broad end point in Figure 4.4.5b. Methyl orange, which changes colour in the pH range 3.1–4.4, would be a more suitable indicator for the second titration.

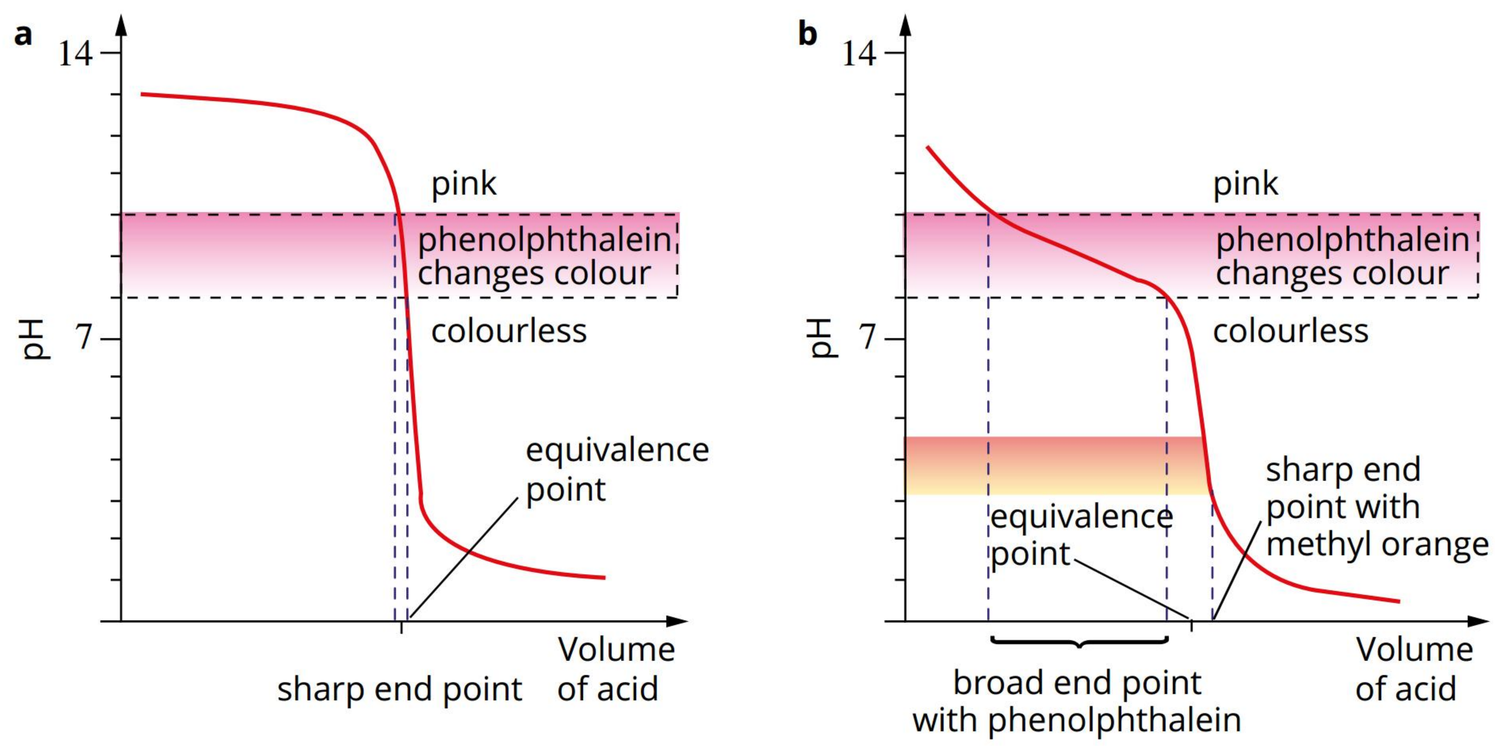


FIGURE 4.4.5 Titration curves showing the pH during a titration of (a) a strong base with a strong acid, and (b) a weak base with a strong acid. Phenolphthalein, which changes colour in the pH range 8.3–10.0, gives a sharp end point in (a) but a broad end point in (b). Methyl orange, which changes colour in the pH range 3.1–4.4, would be a more suitable indicator for the second titration.

Strong acid–strong base titration

The features of the titration curve (Figure 4.4.2 on page 118) for a strong acid-strong base titration are identified and explained on page 118. Recall that the equivalence point occurs when the gradient of the pH curve is steepest. For a reaction between a strong acid and a strong base, the pH at the equivalence point is 7.0. Using an indicator that changes colour within the pH range of the equivalence point results in a sharp end point. Bromothymol blue or phenolphthalein are suitable indicators to use in a strong acid–strong base titration.

Weak acid–strong base titration

The titration curve obtained when a strong base (0.1 mol L^{-1} sodium hydroxide) is added to a weak acid (0.1 mol L^{-1} ethanoic acid) is shown in Figure 4.4.6.

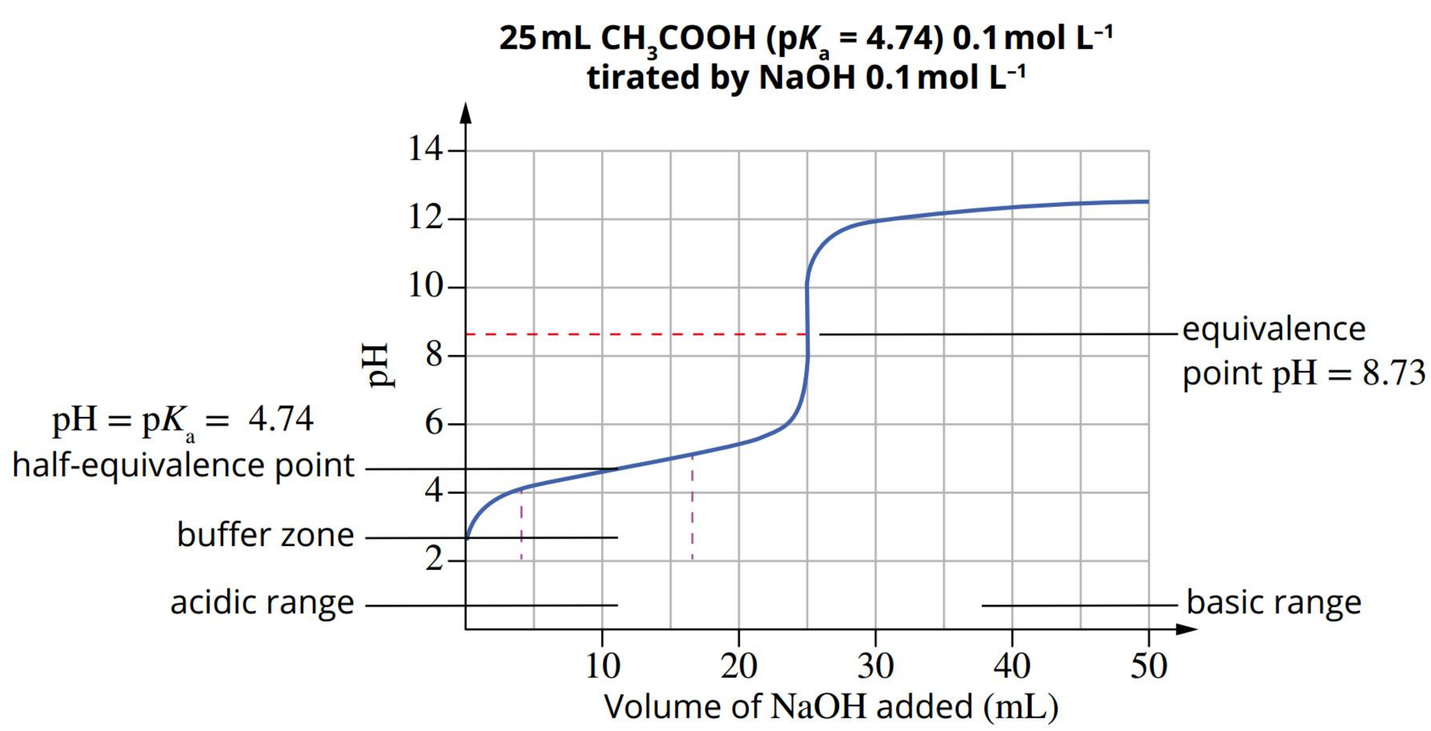


FIGURE 4.4.6 A titration curve for a strong base being added to a weak acid

Features of the titration curve

The shape of the curve reflects the weakly acidic nature of the acid. Before the acid is titrated, the pH of the solution is 2.87. Remember from Chapter 3 that a weak acid, represented by the balanced equation:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

has an acid dissociation constant, K_a, determined using the formula:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Since the ionisation of the weak acid is very small, [HA] can be approximated to be $0.1\,mol\,L^{-1}$.

Thus, for ethanoic acid ($K_a = 1.8 \times 10^{-5}$), the expression rearranges and simplifies to:

$$[H_3O^+]\,[A^-] = K_a \times 0.1$$
$$= 1.8 \times 10^{-6}$$

Since ethanoic acid ionises equally into hydromium ions and ethanoate ions, $[H_3O^+]$ can be calculated by taking the square root of 1.8×10^{-6}, which means $[H^+] = 1.34 \times 10^{-3}\,mol\,L^{-1}$.

Since $pH = -\log_{10}[H_3O^+]$, the hydrogen ion concentration of the original acid solution can be determined to be 2.87.

As sodium hydroxide is added to the solution, the pH increases; however, this region is relatively flat and is known as the **buffer zone**. The buffer zone is the part of the titration curve prior to reaching the equivalence point and is the region in which titrant is added with little change to the pH of the solution. On the graph, it appears as a relatively horizontal (flat) portion of the curve.

Buffer solutions resist the change in pH because of the equilibrium between the acid (HA) and its conjugate base (A^-), as shown in the balanced equation:

$$HA \rightleftharpoons H^+ + A^-$$

> A buffer is a solution of weak acid and conjugate base, or weak base and conjugate acid.

When more base is added to the mixture, the OH^- ions react with the H^+, reducing the concentration of H^+ in the solution. By Le Châtelier's principle, this causes the equilibrium to shift to the right, resulting in more of the ethanoic acid dissociating. Therefore, the hydrogen ion (H^+) concentration decreases by less than the amount expected for the quantity of base added.

Halfway between the start of the titration and the equivalence point is a point where the pH is equal to the pK_a of the weak acid.

Using the balanced equation:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

K_a is defined as:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

By taking $\log_{10}$ of both sides, the expression can be written as:

$$\log_{10}K_a = \log_{10}[H^+] + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

Rearranging the expression gives:

$$-\log_{10}[H^+] = \log_{10}K_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

By definition $-\log_{10}[H^+] = pH$ and $-\log_{10}K_a = pK_a$; therefore, the expression can be written as:

$$pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

Therefore, when $\log_{10}\left(\frac{[A^-]}{[HA]}\right) = 0$, $pH = pK_a$.

This happens when $[HA] = [A^-]$ and is the point halfway to the equivalence point, referred to as the **half-equivalence point**.

The change in pH at the equivalence point is not as large as in the earlier strong acid–strong base titration. An indicator that changes colour within the pH range 6.0–10.0, such as phenolphthalein, would be suitable to identify the end point of such a titration.

The reaction occurring is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$$

In this case, the equivalence point has a pH greater than 7.0 because $NaCH_3COO(aq)$ is present. $NaCH_3COO^-$ is a weak base that undergoes hydrolysis with water to produce hydroxide ions, making the solution slightly basic at that point.

After the equivalence point is reached, and more of the strong base is added, the pH continues to increase up to a maximum of 13.0.

This can be determined using the ionic product of water:

$$K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$

Therefore, a 0.1 mol L^{-1} solution of NaOH, where $[OH^-]$ is 0.1, would have a $[H_3O^+] = 1 \times 10^{-13}$, and thus a maximum pH of 13.0 is achievable.

Strong acid–weak base titration

The titration curve obtained when a strong acid (0.1 mol L^{-1} hydrochloric acid) is added to a weak base (0.1 mol L^{-1} ammonia) is shown in Figure 4.4.7.

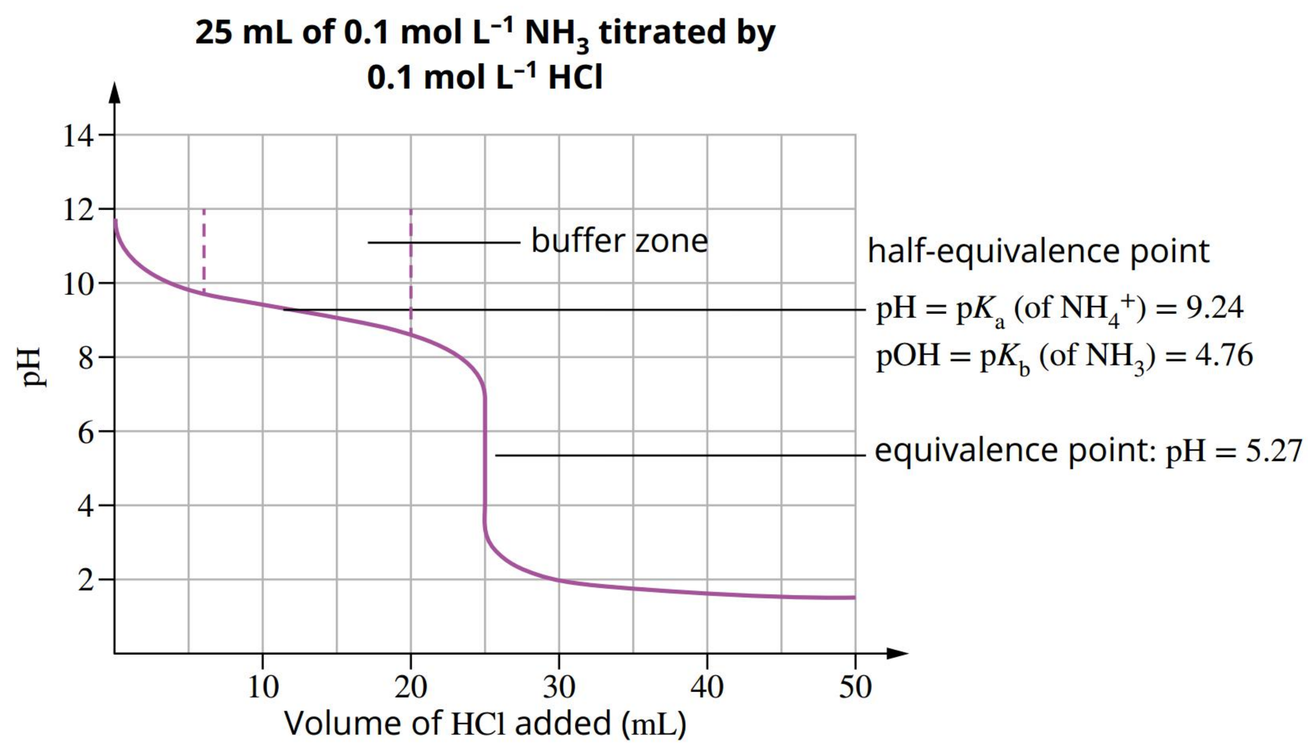


FIGURE 4.4.7 The titration curve for a strong acid added to a weak base

Features of the titration curve

Since aqueous ammonia solution is a weak base ($K_b = 1.75 \times 10^{-5}$), it only partially ionises so $[OH^-]$ is much less than 0.1 mol L^{-1}. Therefore, the pH of the 0.1 mol L^{-1} NH_3 solution is approximately 11.

As with the weak acid–strong base titration, when hydrochloric acid is added to the ammonia solution, the pH decreases slightly. This is the relatively flat (horizontal) region on the titration curve known as the buffer zone.

Buffer solutions resist the change in pH because of the equilibrium between the base (B) and its conjugate acid (BH^+), as shown in the balanced equation:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

When acid (H_3O^+) is added to the equilibrium mixture, it reacts with the hydroxide base (OH^-), consuming the base and pushing the equilibrium to the right, as per Le Châtelier's principle. Consumption of the added acid results in minimal change to pH so long as appreciable amounts of base (B) remain in the equilibrium mixture.

When base (OH^-) is added to the equilibrium mixture, the reaction shifts to the left to consume the added OH^- ions, countering the change to equilibrium, as per Le Châtelier's principle. Once again, this results in minimal change to the pH.

As with the weak acid–strong base titration, halfway between the start of the titration and the equivalence point is a point where the pOH is equal to the pK_b of the weak base.

The dissociation constant, K_b, for the weak base, represented by the equation,

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

is defined as:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

By taking $\log_{10}$ of both sides, the expression can be written as:

$$\log_{10}K_b = \log_{10}[OH^-] + \log_{10}\left(\frac{[BH^+]}{[B]}\right)$$

Rearranging the expression:

$$-\log_{10}[OH^-] = -\log_{10}K_b + \log_{10}\left(\frac{[BH^+]}{[B]}\right)$$

By definition, $-\log_{10}[OH^-] = \text{pOH}$ and $-\log_{10}K_b = \text{p}K_b$; therefore, the expression can be written as:

$$\text{pOH} = \text{p}K_b + \log_{10}\left(\frac{[BH^+]}{[B]}\right)$$

Therefore, when $\log_{10}\left(\frac{[BH^+]}{[B]}\right) = 0$, $\text{pOH} = \text{p}K_b$.

This happens when $[BH^+] = [B]$ and is the point halfway to the equivalence point, referred to as the half-equivalence point.

There is a large drop in pH between about 7.0 and 3.0. Methyl orange would be a suitable indicator for this titration because it changes colour between pH 3.1 and 4.4, which falls within the pH range near the equivalence point. Once again, a sharp end point would be obtained.

The reaction occurring in this instance is:

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

The pH of about 5.0 at the equivalence point can be explained by the presence of the weakly acidic ammonium ion, NH_4^+, when the reaction between HCl and NH_3 is complete.

Figure 4.4.8 compares the titration curves explained in this module.

- Figure 4.4.8(a) represents the titration curve of a strong base–strong acid titration. Point 1 is the pH at the beginning of the titration before any strong acid has been added. Point 2 is the pH at the half-equivalence point when 10 mL of acid has been added. Point 3 is the pH at the equivalence point, where pH = 7. Point 4 is a point past the equivalence point when excess strong acid has been added. Suitable indicators are bromothymol blue and phenolphthalein.
- Figure 4.4.8(b) represents the titration curve of a weak acid–strong base titration. Point 1 is the pH at the beginning of the titration before any strong base has been added. Point 2 is the pH at the half-equivalence point when 10 mL of base has been added and pH = pK_a. Between points 1 and 3 is the buffer zone, where the conjugate acid–base pair are both present. Point 3 is the pH at the equivalence point, where pH > 7. Point 4 is a point past the equivalence point at 30 mL when excess strong base has been added. A suitable indicator is phenolphthalein.
- Figure 4.4.8(c) represents the titration curve of a weak base–strong acid titration. Point 1 is the pH at the beginning of the titration before any strong acid has been added. Point 2 is the pH at the half-equivalence point when 10 mL of acid has been added and pOH = pK_b. Between points 1 and 3 is the buffer zone, where the conjugate acid–base pair are both present. Point 3 is the pH at the equivalence point, where pH < 7. Point 4 is a point past the equivalence point at 30 mL when excess strong acid has been added. A suitable indicator is methyl orange.

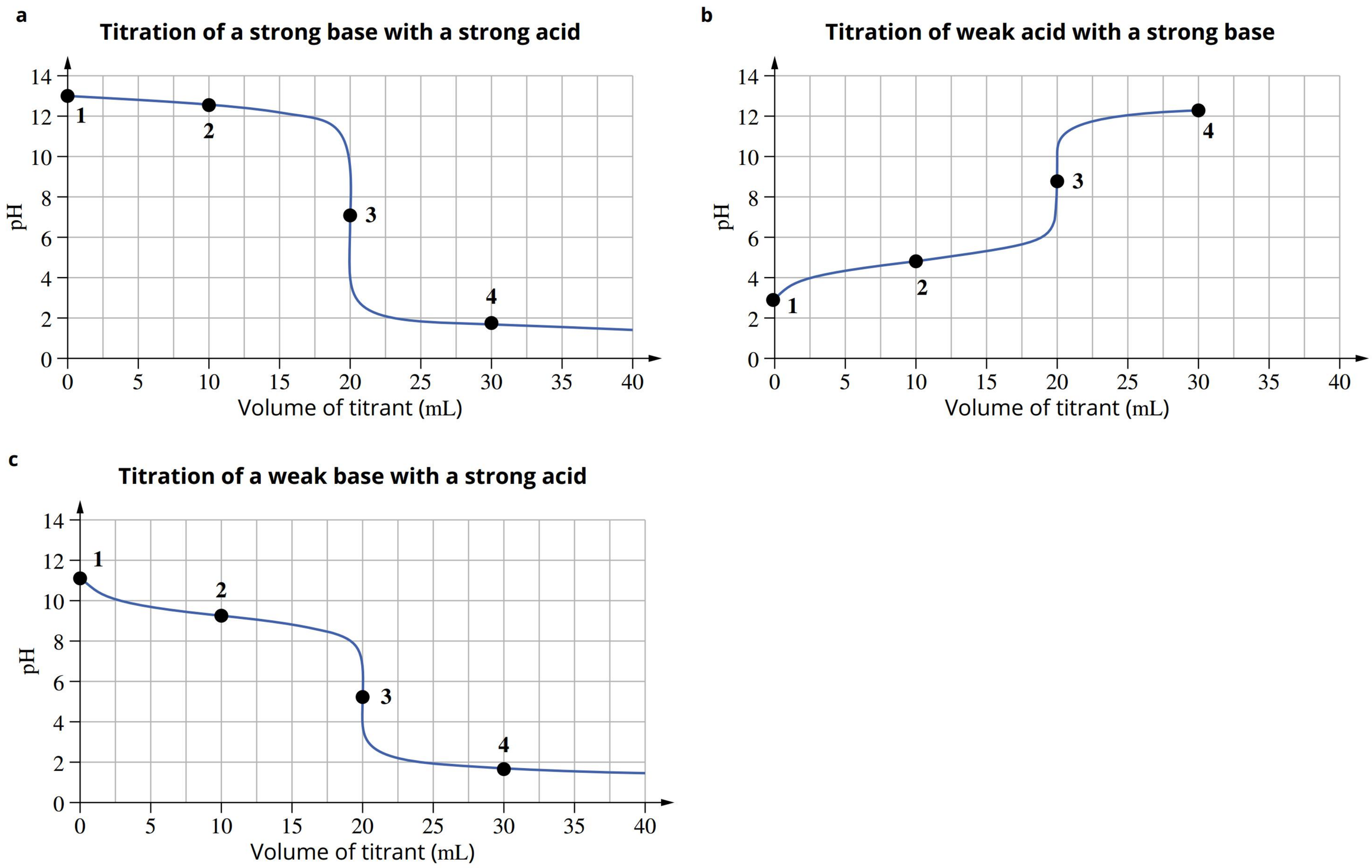
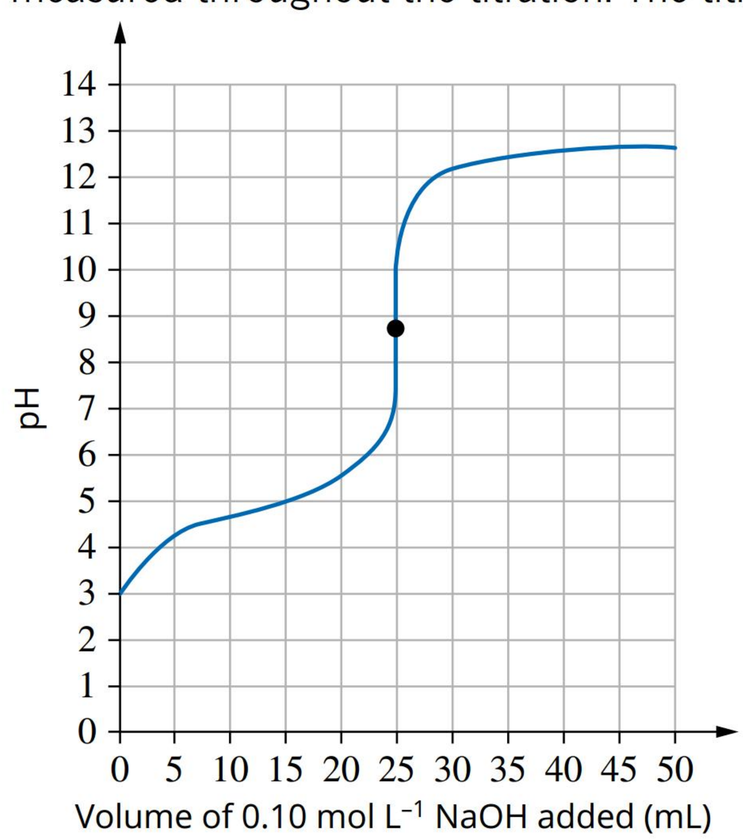


FIGURE 4.4.8 Titration curves obtained during a titration of (a) a strong base with a strong acid, (b) a weak acid with a strong base and (c) a weak base with a strong acid

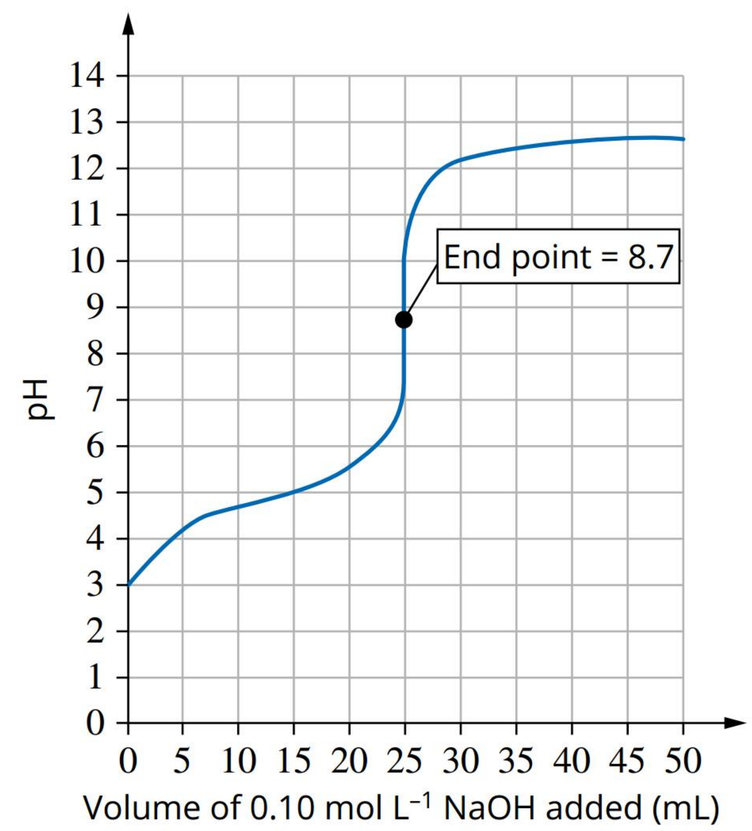
Worked example 4.4.1

A TITRATION CALCULATION USING A pH TITRATION CURVE

The concentration of ethanoic acid (CH_3COOH) in vinegar was determined by titration with a standardised solution of sodium hydroxide. A 25.0 mL aliquot of vinegar was titrated with a 0.12 mol L^{-1} sodium hydroxide solution. The pH was measured throughout the titration. The titration curve is shown below.



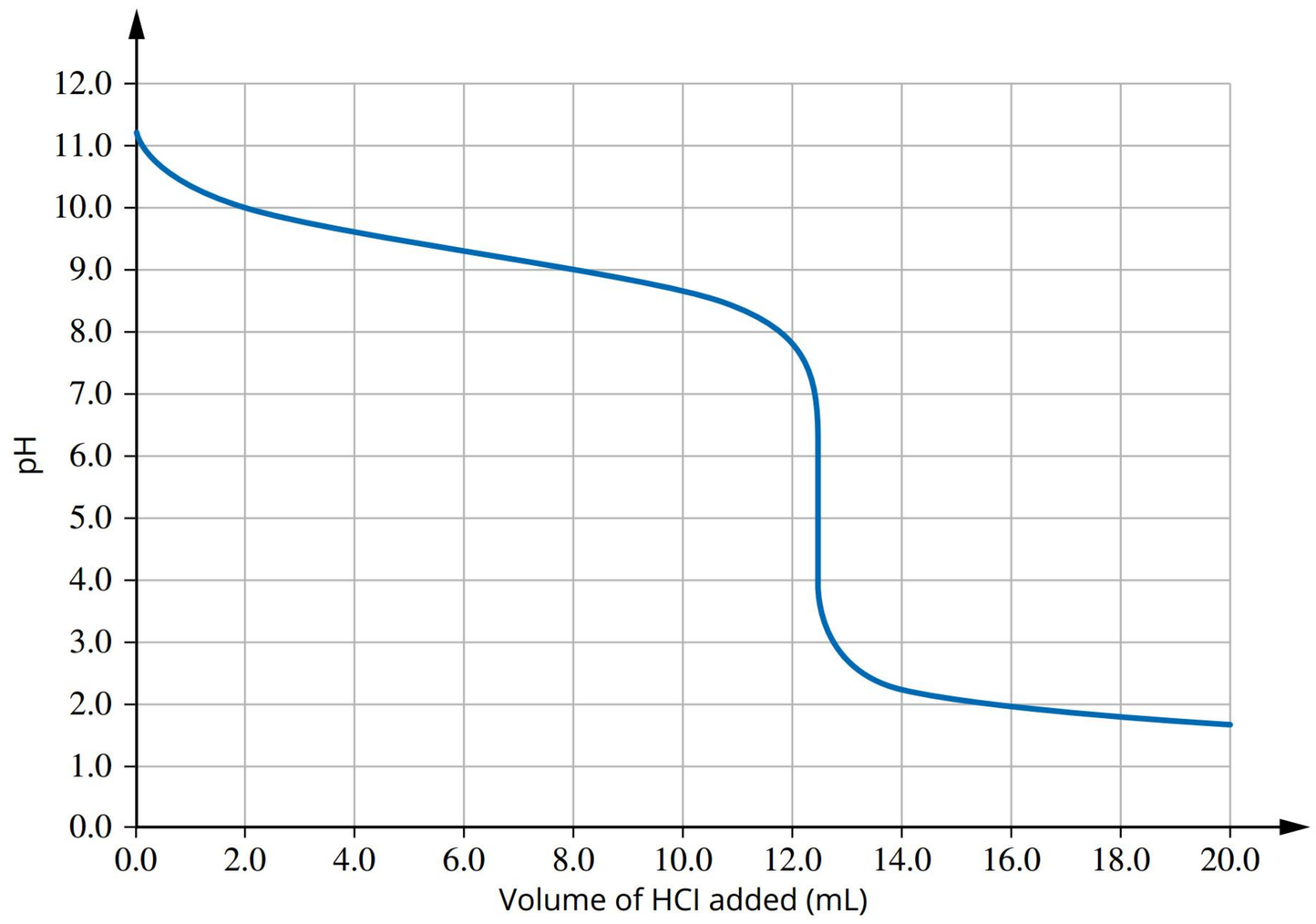
Calculate the concentration, in mol L^{-1}, of ethanoic acid in the vinegar.

Thinking	Working
Identify the end point from the titration curve. Use the end point to determine the titre volume.	 From the titration curve, the end point occurs when the gradient of the pH curve is steepest; at pH 8.7 (vertical axis). The volume of sodium hydroxide added is 25 mL (horizontal axis). Therefore, the sodium hydroxide titre is 25 mL
Write a balanced chemical equation.	$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$
Using the concentration and titre volume of the standard solution, calculate the number of moles of the known substance that reacted in the titration. Remember that volume must be expressed in litres.	$n(NaOH) = cV$ $= 0.12 \times 0.025$ $= 0.0030\,mol$
Use the reactant coefficients in the equation to calculate the number of moles of the unknown solution that reacted in the titration.	$n(CH_3COOH) = n(NaOH)$ $= 0.0030\ mol$
Calculate the concentration of the unknown solution reacting in the titration. Express your answer to the appropriate number of significant figures.	$V(CH_3COOH) = 0.0250\ L$ $c(CH_3COOH) = \frac{n}{V}$ $= \frac{0.0030}{0.0250}$ $= 0.012\,mol\,L^{-1}$ The final result is rounded to 2 significant figures corresponding to the smallest number of significant figures in the original data.

➤ Try yourself 4.4.1

A TITRATION CALCULATION USING A pH TITRATION CURVE

The concentration of ammonia (NH_3) in a cleaning solution was determined by titration with a standardised solution of hydrochloric acid. A 10.0 mL aliquot of cleaning solution was titrated with a 0.092 mol L^{-1} hydrochloric acid solution. The pH was measured throughout the titration. The titration curve is shown below.



Calculate the concentration, in mol L^{-1}, of ammonia in the cleaning solution.

ACID–BASE CONDUCTOMETRIC TITRATIONS

In the previous section, you learnt that a titration curve or pH curve can be used to monitor the progress of an acid–base titration. A **conductometric titration** measures the change in solution **conductivity** against volume of titrant added from a burette. The equivalence point corresponds to a turning point in the change of conductivity during a titration and is determined graphically from a titration curve.

Advantages of conductometric titrations:

- can be used in turbid solutions or even coloured solutions where a visual indicator may not be appropriate
- sensitivity – can be used with very dilute reactants where colour development by visual indicators makes it difficult to detect the end point
- good for applications where the end point is broad, such as a weak acid–weak base titration.

Recall from Units 1 and 2 that for a substance to conduct electricity, it must contain charged particles that are free to move. A solution that conducts electricity by means of the movement of ions is called an electrolyte. Pure water contains very few ions and is a poor conductor of electricity. As the concentration of ions in solution increases, so does the electrical conductivity. It is the flow of ions towards the electrodes that is responsible for the electrical conductivity of electrolyte solutions. Quantitative measurements can be taken if an ammeter is included in the circuit. In an acid–base conductometric titration, the equivalence point of the titration is detected by changes in the electrical conductivity of the solution.

Solution conductivity depends not only on the concentration of ions but also on the identity of ions in the electrolyte, because some ions are more mobile than others in solution. Table 4.4.3 lists the molar conductivity values of cations and anions in aqueous solutions at 25°C. Hydrogen ions, $H^+(aq)$, and hydroxide ions, $OH^-(aq)$, are more mobile than other ions. For a given concentration, solutions containing $H^+(aq)$ and $OH^-(aq)$ will have a higher electrical conductivity than solutions containing other ions.

TABLE 4.4.3 Molar conductivity of cations and anions in aqueous solution at 25°C

Cation	Molar conductivity ($S\,cm^2\,mol^{-1}$)	Anion	Molar conductivity ($S\,cm^2\,mol^{-1}$)
H^+	349.8	OH^-	198.3
K^+	73.5	Br^-	78.1
NH_4^+	73.5	I^-	76.8
Ag^+	61.9	Cl^-	76.3
Na^+	50.1	NO_3^-	71.5
Li^+	38.7	F^-	55.4
Ba^{2+}	126	CH_3COO^-	40.9

You will recall from Chapter 3 that a strong acid is one that fully ionises in water, forming hydrogen ions and its conjugate base. Therefore, solutions of strong acids contain ions with virtually no unreacted acid molecules remaining. A weak acid is one that only partially ionises and can be represented by HA in the following equilibrium equation:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

The dissociation constant (K_a) for weak acids is small; therefore, the position of equilibrium favours the reactants, and there are relatively low concentrations of product ions present. Acids of equal concentrations have different abilities to conduct an electric current. At the same concentration and temperature, aqueous solutions of strong acids are better electrical conductors than aqueous solutions of weak acids. Similarly, at the same concentration and temperature, aqueous solutions of strong bases are better electrical conductors than aqueous solutions of weak bases.

The conductivity of an acid or base solution depends on the:

- concentration of the acid or base – higher concentration results in higher conductivity
- strength of the acid or base – stronger acids and bases have a relatively higher proportion of mobile ions than weaker acids and bases, and therefore generally have a higher conductivity per unit of acid concentration.

Performing an acid–base conductometric titration

In a conductometric titration, the progress of the titration is measured using an ammeter. Figure 4.4.9 shows an example of an apparatus used in the laboratory to perform a conductometric titration. The ammeter provides a measure of the conductivity of the solution. A solution with higher conductivity produces a higher reading on the ammeter.

For example, the beaker in Figure 4.4.9 contains a specified volume of an aqueous solution of a strong acid, HCl, and the burette contains an aqueous solution of a strong base, NaOH. Base from the burette is added 1 mL at a time to the acid in the beaker with stirring, and the ammeter reading is recorded against the total volume of base added. As the concentration of ions changes throughout the titration, the conductivity of the solution in the beaker changes. Conductometric titration determines the equivalence point of the titration based on a turning point in the change of conductivity. To determine the equivalence point, a

conductometric titration curve is constructed by graphing conductivity against the volume of base added. The shape of the titration curve is determined by the strength of both the acid and the base used in the titration.

The equivalence point in a conductometric titration is indicated by a sudden change in conductivity.

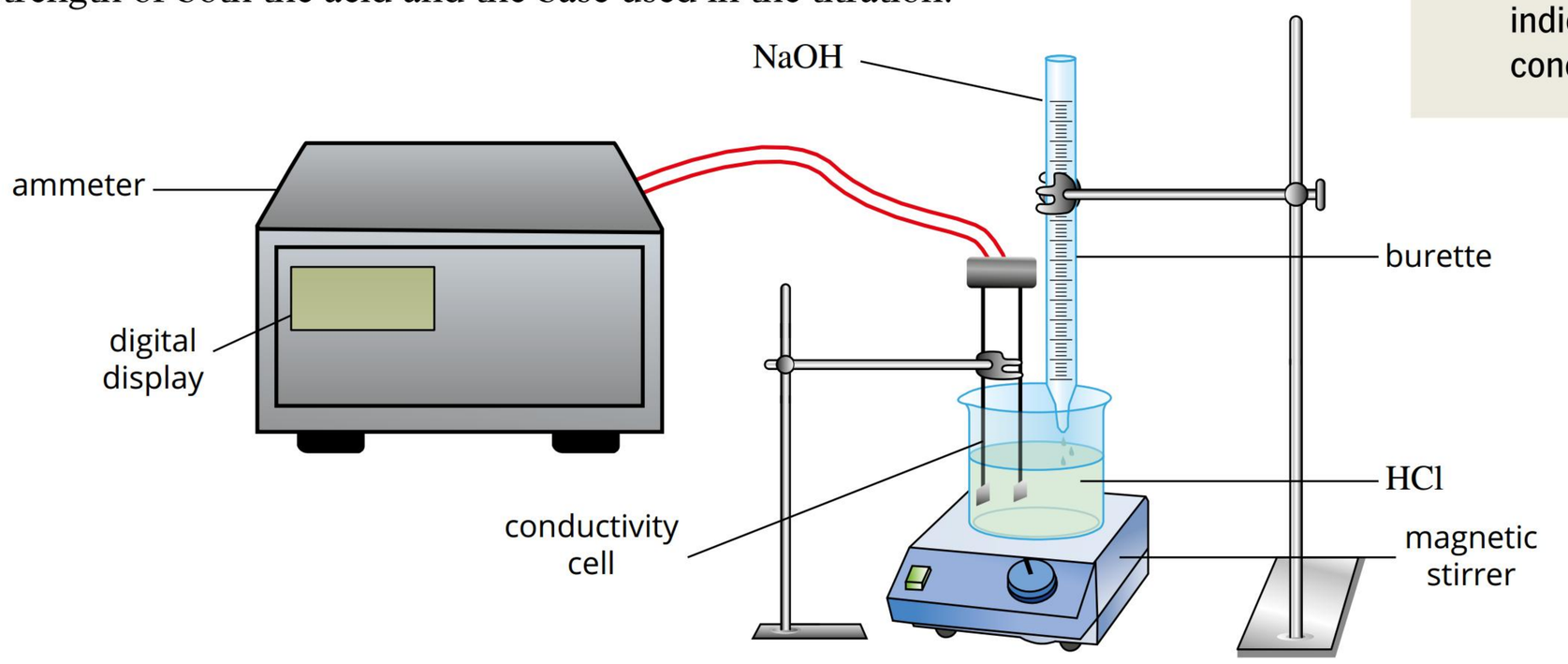


FIGURE 4.4.9 The change in conductivity during an acid–base titration is measured using a conductivity cell attached to a conductivity meter.

Strong acid–strong base conductometric titration

The titration curve obtained when a strong base (e.g. 0.1 mol L^{-1} sodium hydroxide) is added from the burette into a beaker containing a strong acid (e.g. 0.1 mol L^{-1} hydrochloric acid) is shown in Figure 4.4.10. The equation for the reaction is:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

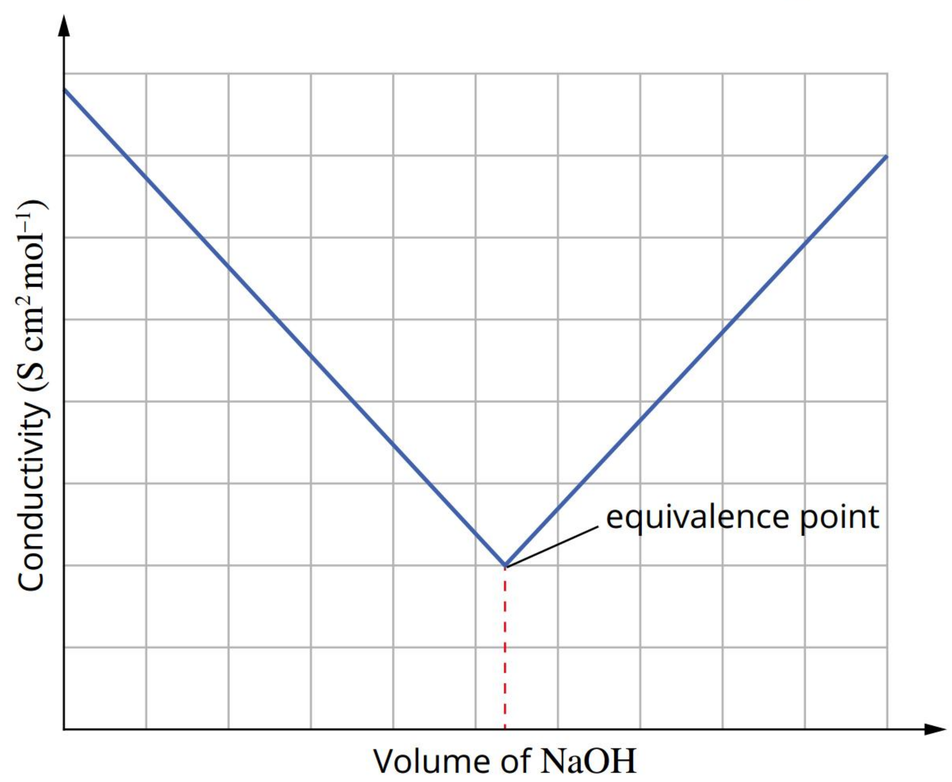


FIGURE 4.4.10 A conductometric curve for the titration of a strong acid (HCl) and a strong base (NaOH)

Initially, the conductivity is relatively high because hydrochloric acid, a strong acid, completely ionises to produce highly mobile H^+ cations and Cl^- anions:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

The conductivity of sodium hydroxide, a strong base, is also high. In aqueous solution, sodium hydroxide completely dissociates to produce Na^+ cations and highly mobile OH^- anions:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

As NaOH(aq) is added from the burette, OH^- ions react with H^+ ions:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The solution in the beaker contains $Na^+(aq)$, $Cl^-(aq)$ and a decreasing number of highly mobile $H^+(aq)$ ions. As the concentration of $H^+(aq)$ gradually decreases with the addition of sodium hydroxide from the burette, the conductivity of the solution decreases.

At the equivalence point, the ions in solution are the less mobile $Na^+(aq)$ and $Cl^-(aq)$, and the conductivity of the solution reaches a minimum value. Past the equivalence point, there is an excess of sodium hydroxide, so the concentration of $Na^+(aq)$ ions and highly mobile $OH^-(aq)$ ions increases, resulting in increasing conductivity.

Features of the titration curve

- The equivalence point of the titration is the point at which the two straight lines on the titration curve intersect (minimum conductivity).
- The titre volume of the strong base required to neutralise all the strong acid is read from the conductivity curve at the equivalence point.

Strong acid–weak base conductometric titration

The titration curve obtained when a weak base (e.g. 0.1 mol L^{-1} ammonia) is added to a strong acid (e.g. 0.1 mol L^{-1} hydrochloric acid) is shown in Figure 4.4.11. The equation for the reaction is:

$$HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

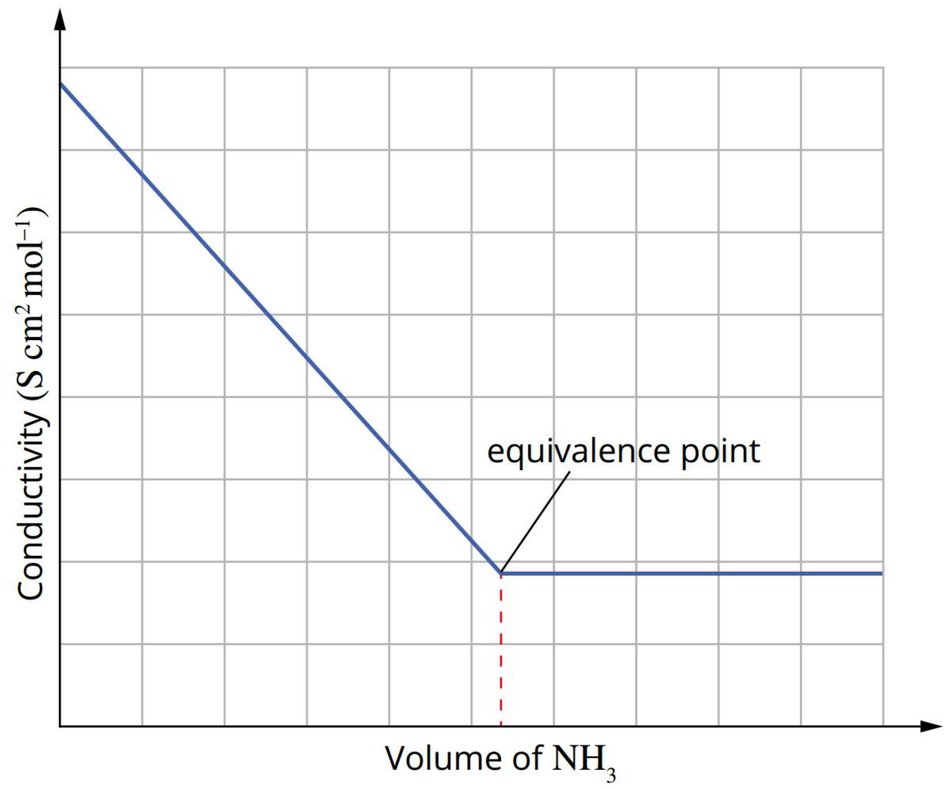


FIGURE 4.4.11 A conductometric curve for the titration of a strong acid with a weak base

Initially, the conductivity is relatively high because hydrochloric acid, a strong acid, completely ionises to produce highly mobile H^+ cations and Cl^- anions:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

The conductivity of ammonia, a weak base, is low. In aqueous solution, ammonia partially ionises to produce relatively low concentrations of NH_4^+ cations and OH^- anions:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = 1.8 \times 10^{-5}\,mol\,L^{-1}$$

As $NH_3(aq)$ is added from the burette, OH^- ions react with H^+ ions present in solution, leading to a decrease in conductivity.

At the equivalence point, the conductivity reaches its minimum value because all the available $H^+(aq)$ ions have been neutralised by the addition of $NH_3(aq)$.

Past the equivalence point, there is an excess of $NH_3(aq)$; however, because the weak base only partially ionises in aqueous solution, the concentration of ions and therefore the conductivity barely changes.

Features of the titration curve

- Conductivity is at a minimum at the equivalence point.
- Past the equivalence point, the titration curve may appear to be almost horizontal.
- The equivalence point of the titration is the point at which the two straight lines on the titration curve intersect.
- The titre volume of the weak base required to neutralise all the strong acid is read from the conductivity curve at the equivalence point.

Weak acid–strong base conductometric titration

The titration curve obtained when a strong base (e.g. 0.1 mol L^{-1} sodium hydroxide) is added from the burette into a beaker containing a weak acid (e.g. 0.1 mol L^{-1} ethanoic acid) is shown in Figure 4.4.12. The equation for the reaction is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq) + H_2O(l)$$

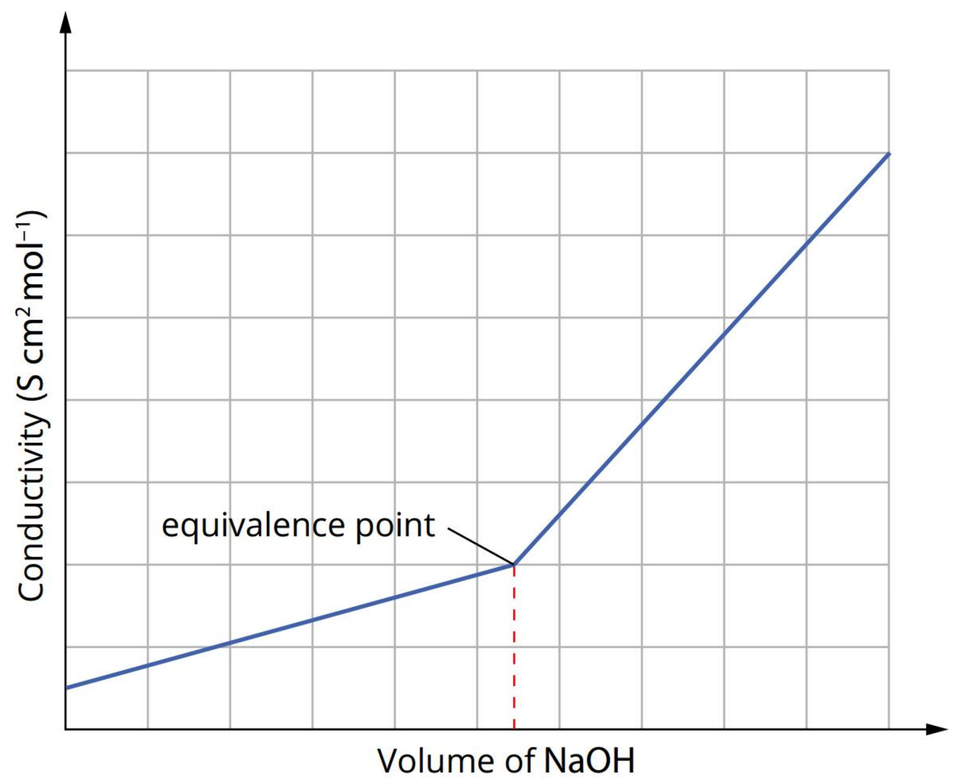


FIGURE 4.4.12 A conductometric curve for the titration of a weak acid with a strong base

Initially, the conductivity is relatively low because ethanoic acid, a weak acid, partially ionises to produce a relatively small concentration of H^+ cations and its conjugate base, ethanoate anions:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq) \quad K_a = 1.8 \times 10^{-5}\,mol\,L^{-1}$$

The conductivity of sodium hydroxide, a strong base, is high. In aqueous solution, sodium hydroxide completely dissociates to produce Na^+ cations and highly mobile OH^- anions:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

As NaOH(aq) is added from the burette, OH^- ions react with the small number of H^+ ions present in solution, leading to a small decrease in conductivity. This small decrease may not be visible on the titration curve.

After the initial number of $H^+(aq)$ ions have been neutralised, the position of equilibrium shifts to the right to produce more $H^+(aq)$ ions and $CH_3COO^-(aq)$ ions (Le Châtelier's principle). These $H^+(aq)$ ions are neutralised by the addition of NaOH(aq); however, the conductivity of the solution increases due to the increased concentration of $CH_3COO^-(aq)$ and $Na^+(aq)$ ions.

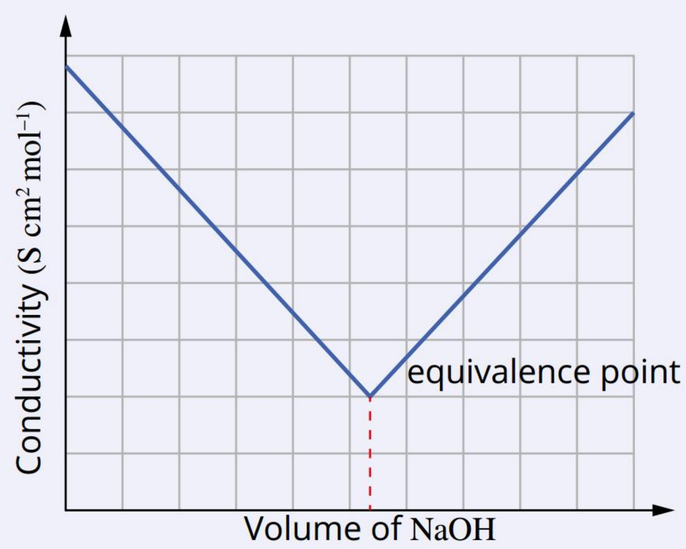
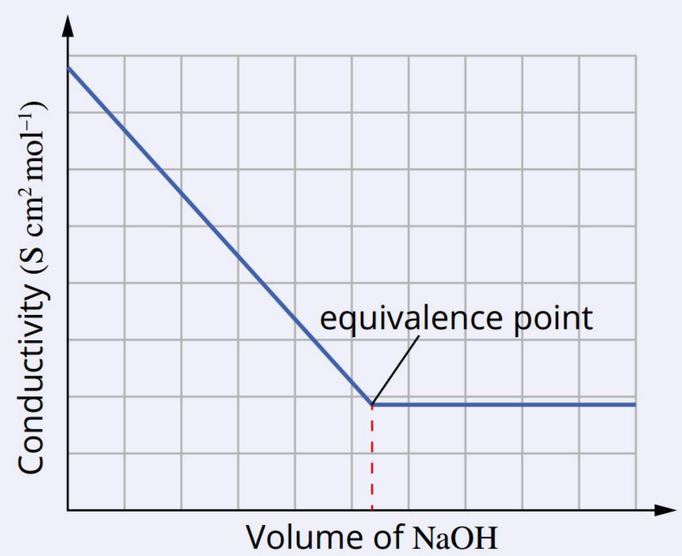
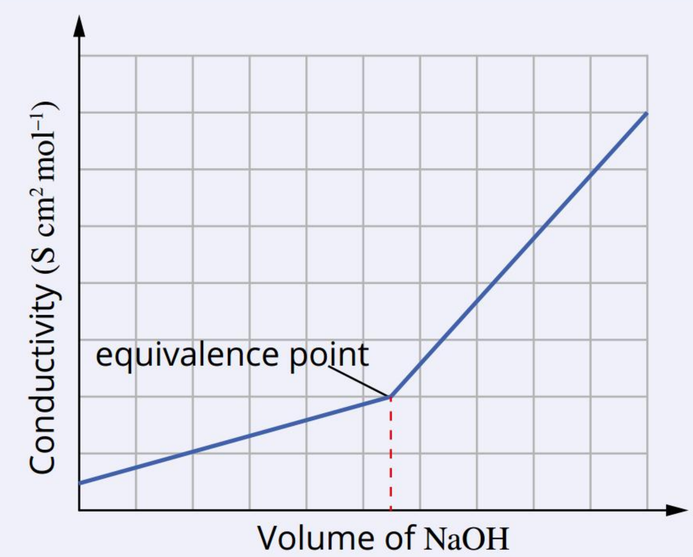
After the equivalence point, the conductivity of the solution increases at a faster rate. This is due to the increased concentration of $Na^+(aq)$ ions, $CH_3COO^-(aq)$ ions and excess $OH^-(aq)$ ions.

Features of the titration curve

- Beyond the initial minimum, the conductivity increases because the initial consumption of H^+ ions drives the weak acid equilibrium to the right, producing more H^+ ions (which are immediately consumed) and CH_3COO^- ions. At the same time, the Na^+ ion concentration increases due to the addition of NaOH. The combination of increasing concentrations of CH_3COO^- ions and Na^+ ions results in a linear increase in conductivity up until the equivalence point is reached.
- Past the equivalence point, the conductivity of the solution increases at a greater rate, as shown by the increased gradient of the graph due to the addition of excess NaOH – resulting in an increase in the highly mobile OH^- ions.
- The equivalence point of the titration is the point at which the gradient of the line increases.
- The titre volume of the strong base required to neutralise all the weak acid is read from the conductivity curve at the equivalence point.

The shapes of the acid–base conductometric titration curves are summarised in Table 4.4.4. The equivalence point of these titrations is indicated by the change in gradient of the conductivity curve where two straight lines intersect. The titre volume is read from the curve at the equivalence point.

TABLE 4.4.4 Typical acid–base conductometric titration curves

Strong acid–strong base	Strong acid–weak base	Weak acid–strong base
		
Well-defined equivalence point at the intersection of two lines	Well-defined equivalence point at the intersection of two lines	Poorly defined equivalence point at the intersection of two positively sloped lines

PRECIPITATION CONDUCTOMETRIC TITRATIONS

Conductometric titrations quantify the amount of reactant present in a given solution by measuring the change in conductivity as a volume of titrant is added from a burette. In a precipitation reaction, the formation of a precipitate removes ions from an electrolyte solution. For example, when a solution of sodium sulfate, $Na_2SO_4(aq)$, is added to a solution of barium nitrate, $Ba(NO_3)_2(aq)$, the sparingly soluble salt, barium sulfate, $BaSO_4(s)$, will be produced via the precipitation reaction represented in the following equation:

$$Na_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$$

When all the $Ba^{2+}(aq)$ ions have been consumed (and incorporated into the solid precipitate), any further addition of $Na_2SO_4(aq)$ will lead to excess $Na^+(aq)$ ions and excess $SO_4^{2-}(aq)$ ions in the solution. The subsequent change in conductivity can be measured in a precipitation conductometric titration.

Recall from Chapter 2 that when a sparingly soluble ionic compound is added to water, an equilibrium is established between the pure solid and a solution of its ions. The **solubility product constant**, K_{sp}, is an equilibrium constant that reflects the extent to which an ionic compound dissolves in water. The more soluble a substance is, the higher the K_{sp} value it has.

Consider the titration of silver nitrate with potassium chloride represented by the equation:

$$AgNO_3(aq) + KCl(aq) \rightarrow KNO_3(aq) + AgCl(s)$$

Potassium chloride, KCl, is a strong electrolyte, dissociating completely in water according to the equation:

$$KCl(s) \rightarrow K^+(aq) + Cl^-(aq)$$

The conductivity of an aqueous solution of potassium chloride is relatively high due to the presence of $K^+(aq)$ and $Cl^-(aq)$ ions.

Silver nitrate, $AgNO_3(aq)$, is also a strong electrolyte, dissociating completely in water according to the equation:

$$AgNO_3(s) \rightarrow Ag^+(aq) + NO_3^-(aq)$$

The conductivity of an aqueous solution of silver nitrate is also relatively high due to the presence of $Ag^+(aq)$ and $NO_3^-(aq)$ ions.

The product, silver chloride (AgCl), is a sparingly soluble ionic compound.

$$AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Ag^+][Cl^-] = 1.77 \times 10^{-10}\,\text{mol}\,\text{L}$$

When $AgNO_3(aq)$ is added to KCl(aq), a white precipitate of AgCl forms, leaving K^+ ions and NO_3^- ions in solution.

A conductometric titration can be used to measure the changes in conductivity during the reaction between KCl(aq) and $AgNO_3(aq)$. Figure 4.4.13 shows the apparatus used to perform a conductometric titration. In this example, the burette contains $AgNO_3(aq)$ and the beaker contains KCl(aq). Before any silver nitrate is added from the burette, the conductivity of the potassium chloride solution in the beaker is relatively high due to the presence of K^+ cations and Cl^- anions.

During the titration, silver nitrate is added, forming sparingly soluble silver chloride, AgCl. The Cl^- ions forming the precipitate are replaced by NO_3^- ions with similar molar conductivities (Table 4.4.3); therefore, the conductivity remains relatively constant until the equivalence point is reached. At the equivalence point, all the KCl has reacted with the $AgNO_3$ added from the burette. After the equivalence point, $AgNO_3$ is in excess, so more $Ag^+(aq)$ and $NO_3^-(aq)$ ions are being added to the solution. As the concentration of ions in solution increases, the conductivity increases. A conductance curve for the titration is shown in Figure 4.4.14.

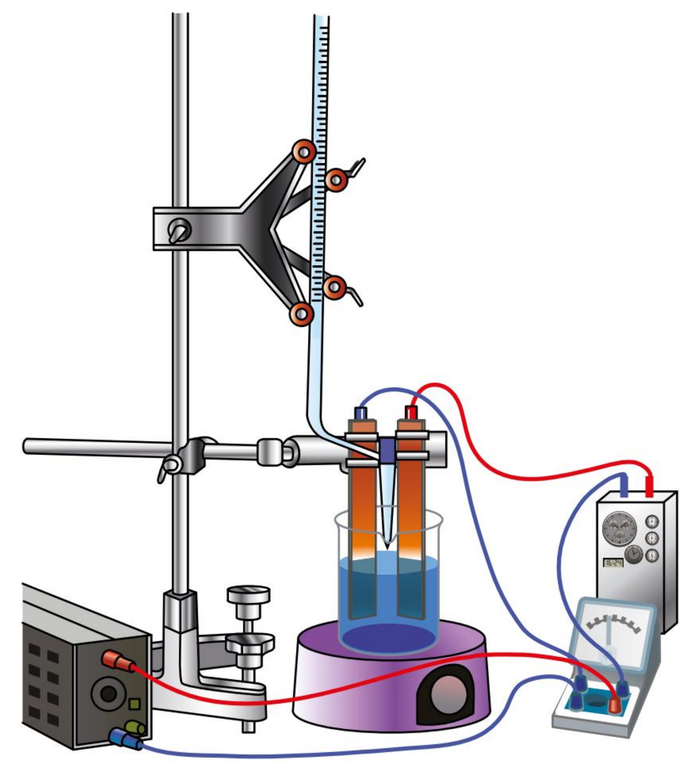


FIGURE 4.4.13 A conductometric titration requires a power supply, conductivity meter and electrodes in a circuit under the burette.

Features of the titration curve

- The equivalence point for the titration is where the two straight lines intersect.
- The titre volume of the silver nitrate solution required to react with the potassium chloride solution is read from the conductivity curve at the end point.

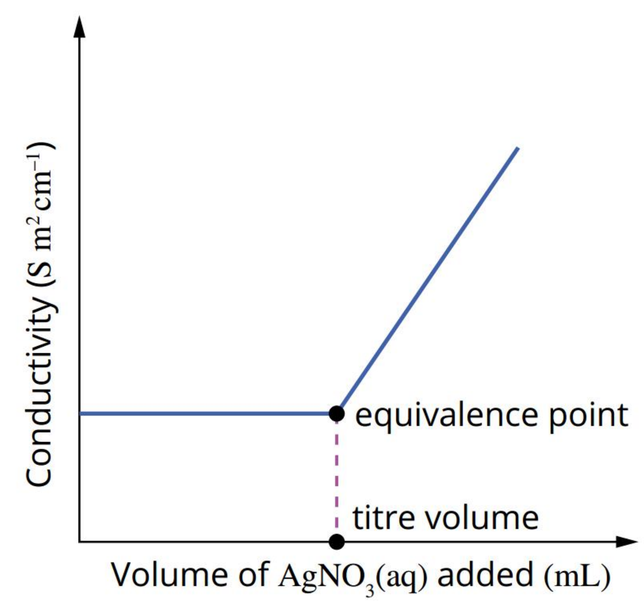


FIGURE 4.4.14 A conductometric titration curve for the reaction between solutions of potassium chloride and silver nitrate

Another example is the acid–base reaction between barium hydroxide and sulfuric acid.

$$Ba(OH)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2H_2O(aq)$$

Barium hydroxide, $Ba(OH)_2$, is highly soluble, dissociating completely in water according to the equation:

$$Ba(OH)_2(s) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

The conductivity of an aqueous solution of barium hydroxide is high due to the presence of $Ba^{2+}(aq)$ ions and the highly mobile $OH^-(aq)$ ions.

Sulfuric acid, $H_2SO_4(aq)$, a strong acid, ionises completely in water according to the equation:

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$

The conductivity of an aqueous solution of sulfuric acid is also relatively high due to the presence of the highly mobile $H^+(aq)$ ions and $HSO_4^-(aq)$ ions.

The product, barium sulfate, is a sparingly soluble ionic compound.

$$BaSO_4(s) \rightarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$$

When $H_2SO_4(aq)$ is added to $Ba(OH)_2(aq)$, the products are a white precipitate of $BaSO_4$ and water.

A conductometric titration can be used to measure the changes in conductivity during the reaction between $Ba(OH)_2(aq)$ and $H_2SO_4(aq)$. In this example, the burette contains $H_2SO_4(aq)$ and the beaker contains $Ba(OH)_2(aq)$. Before any sulfuric acid is added from the burette, the conductivity of the barium hydroxide solution in the beaker is relatively high due to the presence of Ba^{2+} cations and OH^- anions.

Initially, as sulfuric acid is added from the burette, ions are being removed from the solution in order to form both the $BaSO_4$ precipitate and water molecules; therefore, the conductivity decreases until the equivalence point. After the equivalence point, H_2SO_4 is in excess, so more $H^+(aq)$ and $HSO_4^-(aq)$ ions are being added to the solution. As the concentration of ions in solution increases, the conductivity increases. A conductivity curve for the titration is shown in Figure 4.4.15.

Features of the titration curve

- The equivalence point for the titration is where the two straight lines intersect.
- The titre volume of the sulfuric acid solution required to react with the barium hydroxide solution is read from the conductivity curve at the equivalence point.

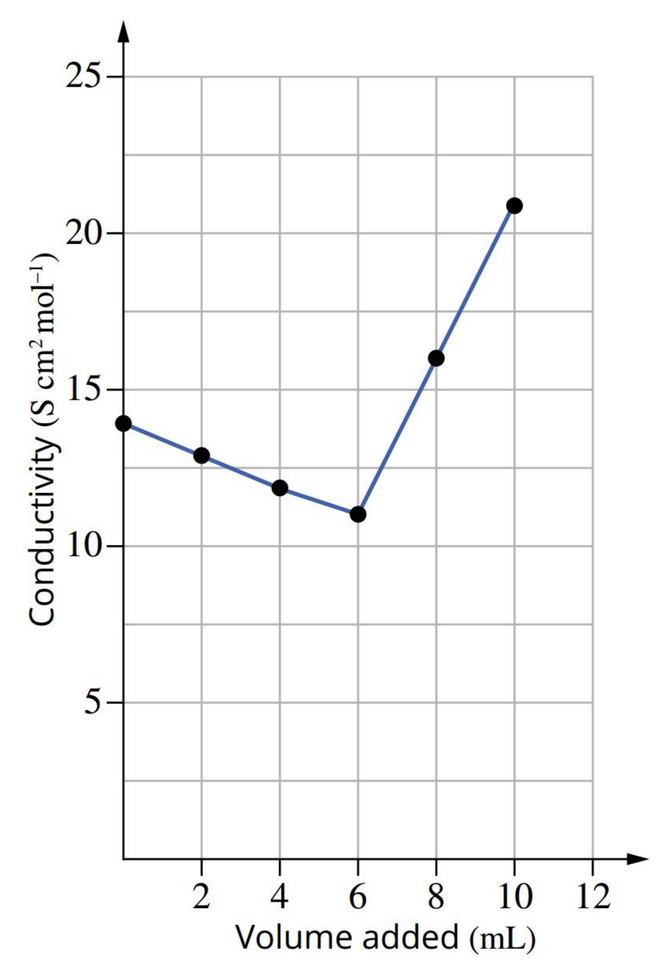


FIGURE 4.4.15 The conductometric titration curve for the reaction between solutions of barium hydroxide and sulfuric acid

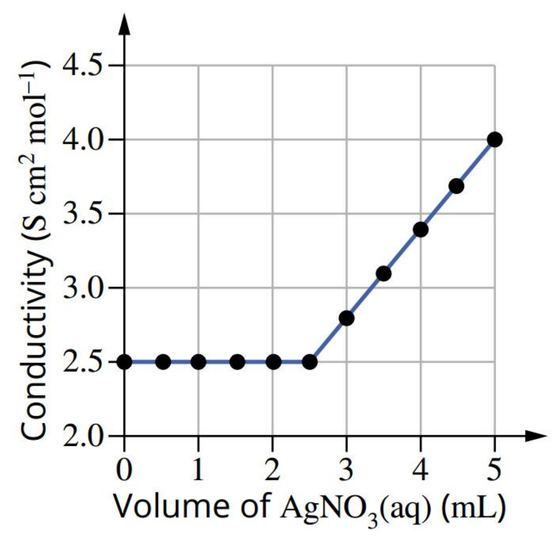
Worked example 4.4.2

A TITRATION CALCULATION USING A TITRATION CURVE

A precipitation conductometric titration was performed to determine the concentration of a potassium chloride solution.

A 15.0 mL aliquot of potassium chloride solution was placed in a beaker. A 0.20 mol L^{-1} standardised silver nitrate solution was gradually added from the burette, and the conductivity changes in the beaker were monitored and recorded. The conductivity measurements were used to construct the titration curve shown below.

Calculate the concentration, in mol L^{-1}, of the potassium chloride solution.

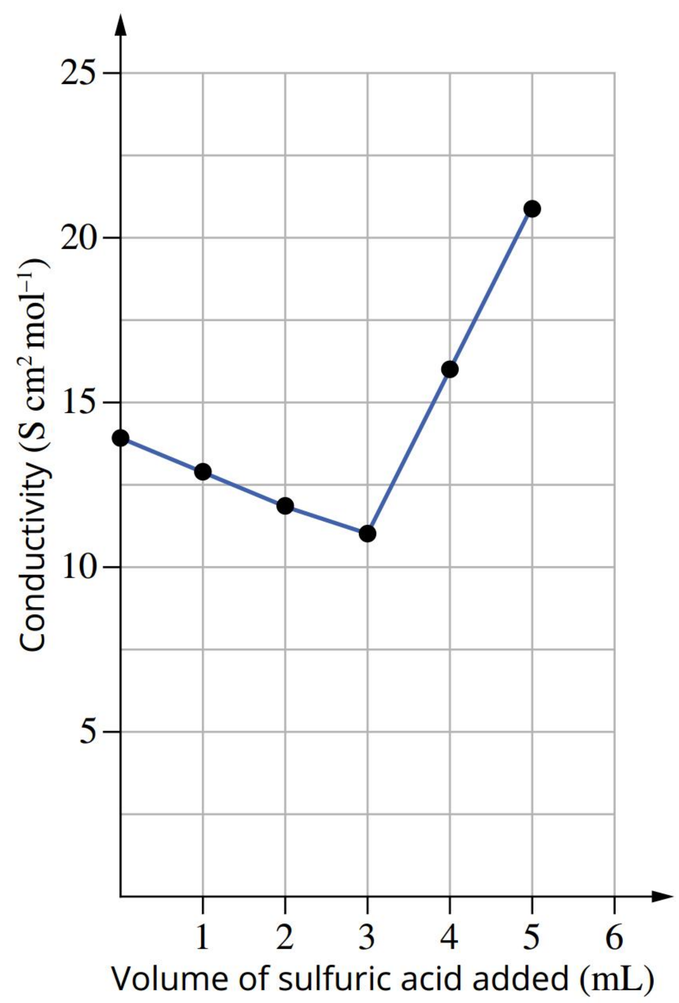
Thinking	Working
Identify the end point from the intersection of the two lines on the titration curve. Use the end point to determine the titre volume.	 From the titration curve, the end point occurs when the volume of silver nitrate added is 2.5 mL (horizontal axis). Therefore, the silver nitrate titre is 2.5 mL
Write a balanced chemical equation.	A precipitation reaction occurs when silver nitrate solution is added to potassium chloride solution: $AgNO_3(aq) + KCl(aq) \rightarrow KNO_3(aq) + AgCl(s)$
Using the concentration and titre volume of the standard solution, calculate the number of moles of the known substance that reacted in the titration. Remember that volume must be expressed in litres.	$n(AgNO_3) = cV$ $= 0.20 \times 0.0025$ $= 0.00050$ mol
Use the reactant coefficients in the equation to calculate the number of moles of the unknown solution that reacted in the titration.	$n(KCl) = n(AgNO_3)$ $= 0.00050$ mol
Calculate the concentration of the unknown solution reacting in the titration. Express your answer to the appropriate number of significant figures.	$V(KCl) = 0.015$ L $c(KCl) = \frac{n}{V}$ $= \frac{0.00050}{0.015}$ $= 0.033$ mol L^{-1} The final result is rounded to 2 significant figures corresponding to the smallest number of significant figures in the original data.

➤ Try yourself 4.4.2

A TITRATION CALCULATION USING A TITRATION CURVE

A precipitation conductometric titration was performed to determine the concentration of a barium hydroxide solution.

A 50.0 mL aliquot of barium hydroxide solution was placed in a beaker. A standardised 0.95 mol L^{-1} sulfuric acid solution was gradually added from the burette, and the conductivity changes in the beaker were monitored and recorded. The conductivity measurements were used to construct the titration curve shown below.



Calculate the concentration, in mol L^{-1}, of the barium hydroxide solution.

4.4 Review

SUMMARY

- Titration curves can be constructed for acid–base titrations by monitoring the pH of the solution and plotting pH values against volume of added titrant.
- pH meters can be used to produce a graph that shows the change in pH of the solution in the conical flask during an acid–base titration, called the titration curve or pH curve.
- The equivalence point occurs when the gradient of the pH curve is steepest.
- The titre volume is determined from the horizontal axis of the pH curve at the equivalence point.
- The shape of a pH curve depends on the strength and concentration of the acids and bases involved.
- pH curves can be used to identify the equivalence point of acid–base titrations.
  - For a strong acid–strong base titration, pH = 7 at the equivalence point.
  - For a weak acid–strong base titration, pH > 7 at the equivalence point.
  - For a strong acid–weak base titration, pH < 7 at the equivalence point.
- The half-equivalence point is the point halfway to the equivalence point and occurs when $[HA] = [A^-]$.
- The buffer zone is the part of the titration curve prior to reaching the equivalence point and is the region in which titrant is added with little change to the pH of the solution.

Continued over page

4.4 Review *continued*

- Titration curves can be constructed by monitoring changes in conductivity versus volume of added titrant.
- Conductometric titration curves can be used to analyse acid–base titrations and precipitation titrations.
- In a precipitation reaction, a sparingly soluble ionic compound with a low solubility product constant, K_{sp}, forms the precipitate.
- The equivalence point corresponds to a turning point in the change of conductivity and is determined graphically.
- For acid–base conductometric titrations, conductivity changes are determined by the strength of the acid and base used in the titration.
- The shapes of some typical acid–base conductometric titration curves are summarised in Table 4.4.4 on page 132.
- The equivalence point of the conductometric titration is the point at which the two straight lines on the titration curve intersect.
- The titre volume is read from the conductivity curve at the equivalence point.

KEY QUESTIONS

Describe

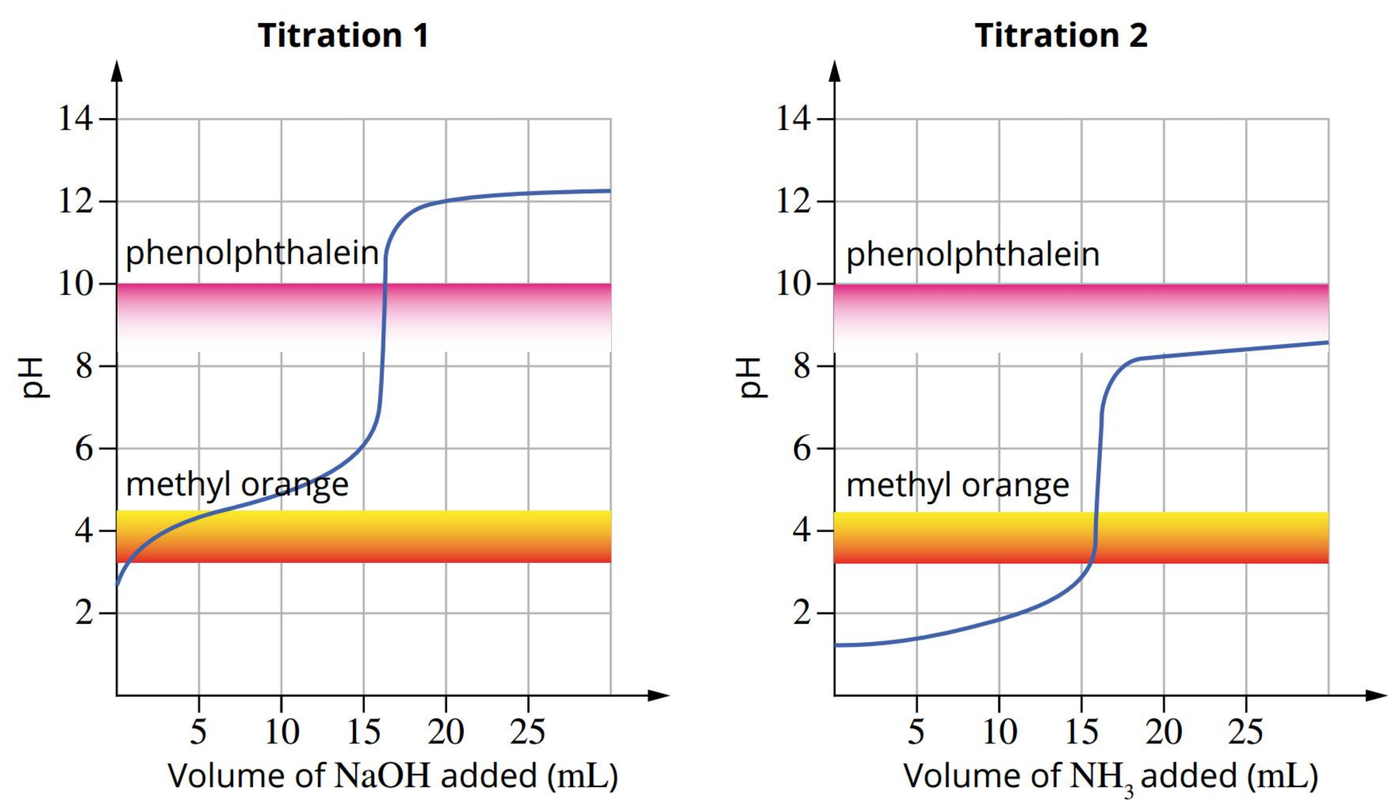
1 For each of the following titrations, identify:
- the species present at the equivalence point
- the pH of the reaction mixture at the equivalence point (7, >7 or <7)
- an appropriate indicator from Table 4.3.1 on page 115.

a The titration of a NaOH solution with an HNO_3 solution

b The titration of a Na_2CO_3 solution with an HCl solution

c The titration of a KOH solution with a CH_3COOH solution

2 A student used a pH meter to produce titration curves for two different acid–base reactions. The range in which two indicators change colour was then superimposed on each graph as shown below. Determine which indicator is best used for each titration.



Apply

3 A student performed a precipitation conductometric titration to determine the concentration of a silver nitrate solution. The experiment involved preparing a sodium chloride standard solution. An accurately measured aliquot of sodium chloride solution was then titrated with silver nitrate from the burette. The experiment results are shown in the table below.

Volume of silver nitrate (mL)	Conductivity (S cm^2 mol^{-1})	Volume of silver nitrate (mL)	Conductivity (S cm^2 mol^{-1})
0.00	1671	11.85	1378
1.95	1618	13.85	1396
3.90	1566	16.85	1557
5.95	1516	17.95	1722
7.95	1467	19.87	1865
9.85	1423	22.05	2024

a Write the balanced equation for the precipitation reaction between sodium chloride and silver nitrate.

b Determine the volume of silver nitrate required to reach the equivalence point. Explain your reasoning.

4 During a titration of sodium hydroxide with ethanoic acid, the solution in the conical flask changed from pink to colourless after 20 mL of the solution in the burette had been added.

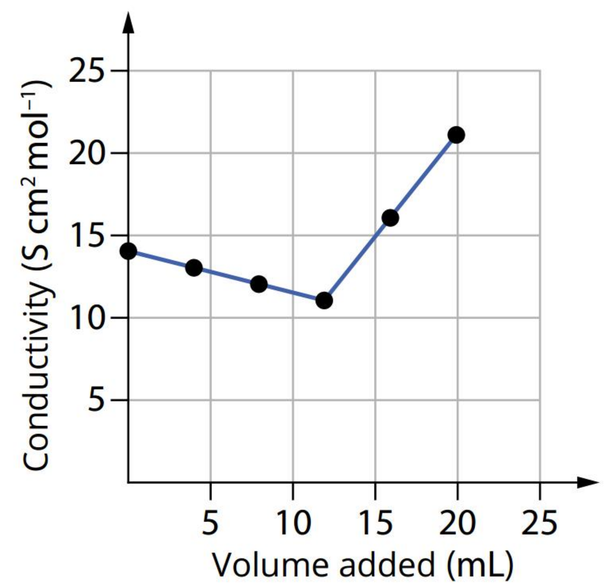
a Determine the most likely indicator used.

b Explain if the pH is progressively increasing or decreasing during the titration.

c When equal amounts of the acid and base have been mixed, deduce what the pH of the solution will be. Determine if it will be less than 7, greater than 7 or equal to 7. Explain your answer.

Analyse

5 A solution containing barium ions is added to a burette. A 20.00 mL aliquot of 0.14 mol L^{-1} sulfuric acid is added to the beaker under the burette. Electrodes are added to the beaker to allow the conductivity of the beaker contents to be recorded. The conductivity graph obtained during the titration is shown below.



a Write an ionic equation for the reaction occurring in the beaker.

b Explain why the conductivity drops initially.

c Explain why the conductivity rises after the equivalence point.

d Calculate the concentration, in mol L^{-1}, of the barium ions.

Chapter review

04

KEY TERMS

accurate
acid–base indicator
aliquot
average titre
buffer zone
burette
concordant titres
conductivity
conductometric titration
conductometric titration curve
dilution factor
end point
equivalence point
excess reactant
half-equivalence point
indicator
indicator range
limiting reactant
mistake
mole ratio
neutralisation reaction
parallax error
pH curve
pipette
precise
primary standard
quantitative analysis
random error
sharp end point
solubility product constant
solution stoichiometry
standard solution
standardised
systematic error
titration
titration curve
titre
transition point
uncertainty
universal indicator
volumetric analysis
volumetric flask

KEY QUESTIONS

Describe

1 A solution is yellow in both bromothymol blue and methyl orange. Select which one of the following is the most accurate approximation of the pH of this solution.

A between 3.1 and 6.0 **B** between 3.1 and 7.6
C between 4.4 and 7.6 **D** between 4.4 and 6.0

2 The acid form of alizarin yellow is yellow, whereas its base form is red. At pH 11.0, the concentrations of the indicator and its conjugate base are equal. Select which one of the following statements about alizarin yellow is correct.

A Alizarin yellow changes colour at exactly pH 11.0.
B A solution of alizarin yellow at pH 11.0 is neutral.
C The indicator can be used to distinguish between a solution of pH 10.0 and a solution of pH 12.0.
D The indicator can be used to distinguish between a solution of pH 10.9 and a solution of pH 11.1.

3 The transition point of the colour change of a weak acid indicator occurs when

A $[In^-] = [H^+]$ **B** $[In^-] = [HIn]$
C $[H^+] = [OH^-]$ **D** $[HIn] = [OH^-]$

4 The acid form of an indicator is blue, and the base form is red. It is purple when there are equal amounts of acid and conjugate base. The general form of the acid–base equation for the indicator is:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

Drops of a purple solution of the indicator are added to 1.0 mol L^{-1} NaOH solution. Select which one of the following correctly identifies the direction of the equilibrium shift and the colour of the resulting solution.

A left, red **B** left, blue
C right, red **D** right, blue

5 Sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) is used as a primary standard in volumetric analysis. Some properties of sodium borate are listed below. Identify which one of these properties is not important in the use of sodium borate as a primary standard.

A It is highly soluble in water.
B Its purity is greater than 99.5%.
C It is a soft, white, crystalline solid.
D It has a molar mass of 381 g mol^{-1}.

6 Referring to Figure 4.3.2 on page 112, identify at what pH range you would expect:

a methyl violet to appear yellow
b phenolphthalein to appear pink
c methyl red to transition from red to yellow.

7 Determine which of the following indicators could be used in a titration in which the equivalence point is between pH 7.0 and pH 13.0.

	Indicator	pH range over which colour changes
I	methyl orange	3.1–4.4
II	methyl red	4.4–6.2
III	bromothymol blue	6.0–7.6
IV	phenolphthalein	8.3–10.0

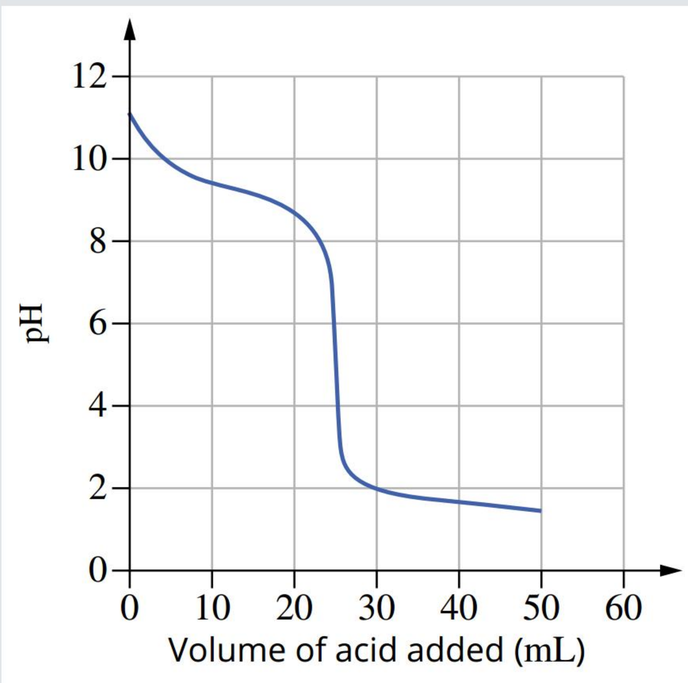
A I only **B** III only
C IV only **D** I and II only

8 A standard solution of hydrochloric acid (HCl) is titrated four times against a sodium hydroxide (NaOH) solution. The following titres were obtained: 21.05 mL, 20.75 mL, 20.65 mL and 20.75 mL.
The average titre is then calculated and used to determine the concentration of the NaOH. Select the correct value for the average titre.

A 20.65 mL
B 20.72 mL
C 20.75 mL
D 20.80 mL

9 The concentration of battery acid can be determined by titrating a sample of it with a standard solution of a suitable base. Battery acid is sulfuric acid. Identify a primary standard that would be suitable to use to make a standard solution for a successful volumetric analysis.

10 The graph below shows the pH change occurring during an acid–base titration. Identify a solution, at a concentration of 0.01 mol L^{-1}, that is most likely to be present in the conical flask for this titration.

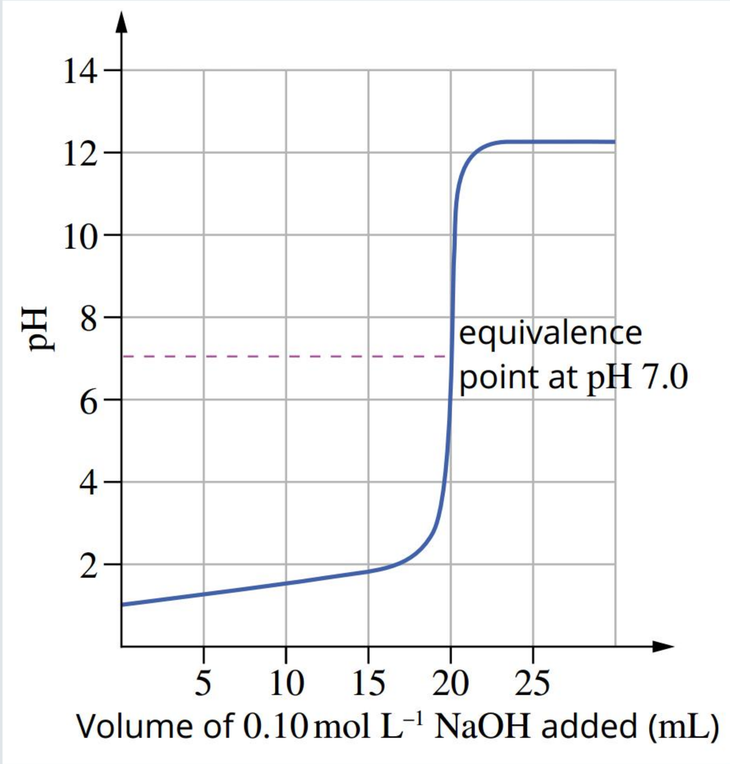


11 A student wishes to determine the concentration of hydrochloric acid using sodium carbonate. List the steps required to accurately determine the concentration of hydrochloric acid using volumetric analysis.

12 Explain the term 'transition point' in terms of K_a using methyl orange as an example.

Apply

13 The titration curve in the graph below shows the change in pH as a solution of 0.10 mol L^{-1} sodium hydroxide (NaOH) is added to a 20.00 mL solution of 0.10 mol L^{-1} hydrochloric acid (HCl).



The titration is repeated using a 0.20 mol L^{-1} NaOH solution. Select the correct statement about the second titration.

A The equivalence point occurs when 10 mL of NaOH is added, and the pH is then 7.0.
B The equivalence point occurs when 40 mL of NaOH is added, and the pH is then 7.0.
C The equivalence point occurs when 10 mL of NaOH is added, and the pH is then greater than 7.0.
D The equivalence point occurs when 40 mL of NaOH is added, and the pH is then greater than 7.0.

14 Determine the concentration of a standard solution of hydrated oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) prepared by dissolving 25.21 g of hydrated oxalic acid in 250.0 mL of deionised water.

15 Determine the mass of sodium carbonate (Na_2CO_3) required to make a 500.0 mL standard solution of 0.400 mol L^{-1} Na_2CO_3.

16 Determine the volume of 0.200 mol L^{-1} KOH required to react with 30.0 mL of 0.100 mol L^{-1} HNO_3.

17 20.0 mL of a 1.00 mol L^{-1} solution of hydrochloric acid (HCl) reacts with 16.0 mL of a 1.00 mol L^{-1} solution of potassium carbonate (K_2CO_3).

a Calculate the number of moles of HCl involved in the reaction.
b Calculate the number of moles of K_2CO_3 involved in the reaction.
c Identify the reactant that is in excess.
d Calculate by how many moles this reactant is in excess.

18 A student performs two titrations:

- A 20.00 mL solution of a weak base is titrated with a 0.10 mol L^{-1} solution of HCl.
- A 20.00 mL solution of a strong base of the same concentration is also titrated with a 0.10 mol L^{-1} solution of HCl.

Explain the difference between the two titrations by discussing the pH of the initial base used in each titration and the titre volume required.

19 The concentration of ethanoic acid, CH_3COOH, in a vinegar solution was determined by titration with a standardised solution of 1.08 mol L^{-1} sodium hydroxide, NaOH. A 25.00 mL aliquot of vinegar is added to the sodium hydroxide solution. Titres of 24.05, 22.10, 22.05 and 22.00 mL were required to reach the end point. Determine the concentration of ethanoic acid, in mol L^{-1}, in the vinegar.

Analyse

20 18.1 mL of a 0.0988 mol L^{-1} phosphoric acid solution, H_3PO_4, is added to 25.3 mL of a 0.114 mol L^{-1} barium hydroxide solution, $Ba(OH)_2$. The equation for the reaction is:

$$2H_3PO_4(aq) + 3Ba(OH)_2(aq) \rightarrow Ba_3(PO_4)_2(s) + 6H_2O(l)$$

a Determine the limiting reactant.

b Calculate the mass of barium phosphate precipitate in the reaction mixture when the reaction is complete.

21 15.0 mL of a 2.00 mol L^{-1} solution of lithium hydroxide (LiOH) is added to 25.0 mL of a 0.400 mol L^{-1} solution of nitric acid (HNO_3). The equation for the reaction that occurs is:

$$HNO_3(aq) + LiOH(aq) \rightarrow LiNO_3(aq) + H_2O(l)$$

a Determine which reactant is the limiting reactant.

b Calculate the mass of lithium nitrate ($LiNO_3$) in the reaction mixture when the reaction is complete.

22 Solutions of the acid–base indicator neutral red, represented by the formula HIn, contain an equilibrium mixture of the red-coloured acid form of the indicator and an amber-coloured conjugate base form.

a Write an equation to represent the equilibrium between HIn and its conjugate base form.

b Determine the colour of the indicator in 0.1 mol L^{-1} HCl.

23 A standard solution of potassium carbonate (K_2CO_3) is made by adding 1.227 g of K_2CO_3 to a 250.0 mL volumetric flask and filling to the mark with water. 20.00 mL aliquots are taken and titrated against a sulfuric acid solution using methyl orange indicator. The average titre was 22.55 mL of sulfuric acid.

a Write the balanced equation for the reaction.

b Calculate the concentration, in mol L^{-1}, of the K_2CO_3 solution.

c Calculate the concentration, in mol L^{-1}, of the sulfuric acid solution.

24 The results for a conductivity titration are provided in the table below. In this titration, the conductivity of the reaction mixture is measured when a 0.50 mol L^{-1} sodium hydroxide solution is progressively added to 10.0 mL of a hydrochloric acid solution of unknown concentration.

Volume NaOH (mL)	Conductivity (mS cm^2 mol^{-1})	Volume NaOH (mL)	Conductivity (mS cm^2 mol^{-1})
0	30.0	10	11.67
1	27.5	11	12.50
2	25.0	12	13.33
3	22.5	13	14.17
4	20.0	14	15.00
5	17.5	15	15.83
6	15.0	16	16.67
7	12.5	17	17.50
8	10.0	18	18.33
9	10.8	19	19.17
		20	20.00

a Use the data provided to draw a titration curve.

b Calculate the concentration of the hydrochloric acid solution.

c Identify the factors that affect conductivity.

25 **a** Outline the difference between volumetric titration and conductometric titration.

b Describe two situations in which the use of a conductivity titration is preferable to using a volumetric titration using an indicator.

26 1.104 g of sodium carbonate (Na_2CO_3) is dissolved in water in a 250.0 mL volumetric flask. 20.00 mL aliquots of this solution were titrated with nitric acid (HNO_3). An average titre of 23.45 mL was found.

a Determine the concentration, in mol L^{-1}, of the Na_2CO_3 solution.

b Calculate the concentration, in mol L^{-1}, of the HNO_3 solution.

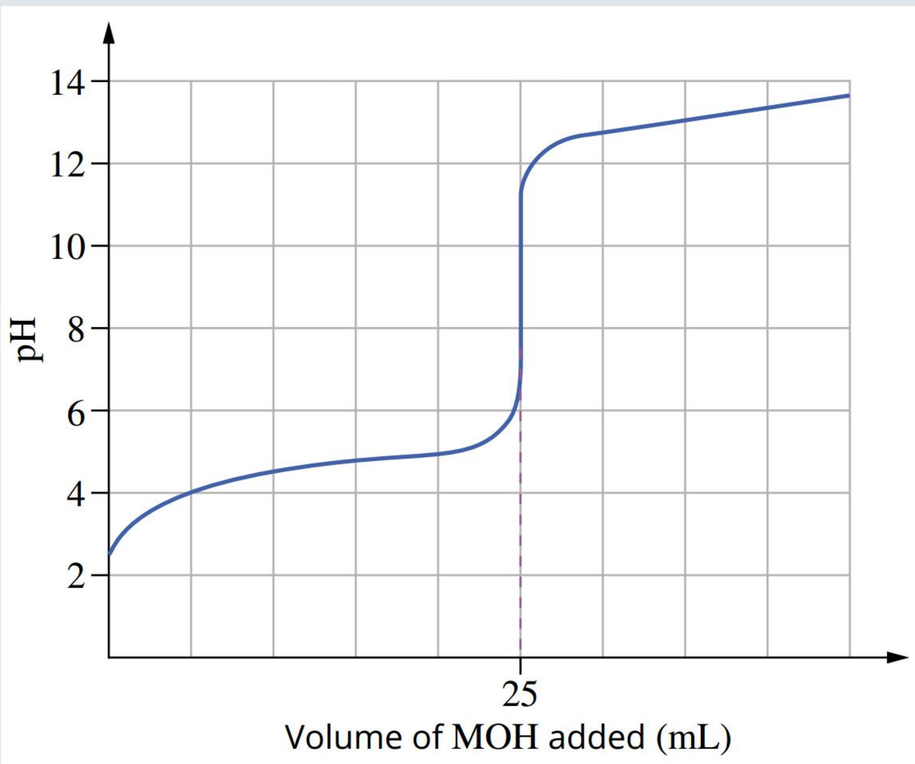
27 A chemistry student is required to accurately determine the concentration of a solution of hydrochloric acid. First, the student makes up 250.0 mL of a standard solution of sodium carbonate (Na_2CO_3). This solution contains 1.358 g of Na_2CO_3. Next, the student takes a 20.00 mL aliquot of this standard solution and titrates it against the hydrochloric acid. An average titre of 20.25 mL of hydrochloric acid was required to reach the end point.

- **a** Write a balanced equation for the reaction between the sodium carbonate and hydrochloric acid solutions.
- **b** Determine the concentration, in mol L^{-1}, of the sodium carbonate solution.
- **c** Calculate the concentration, in mol L^{-1}, of the hydrochloric acid solution.
- **d** If sulfuric acid of the same concentration as the hydrochloric acid was used instead of the hydrochloric acid, predict the effect this would have had on the volume of acid required for the titration.

28 A student titrated an aliquot of standard sodium carbonate solution with hydrochloric acid in a burette. Deduce whether the concentration determined for the hydrochloric acid would be higher, lower or unchanged compared to the actual value if the following apparatus had been washed with deionised water, but not dried, directly before use.

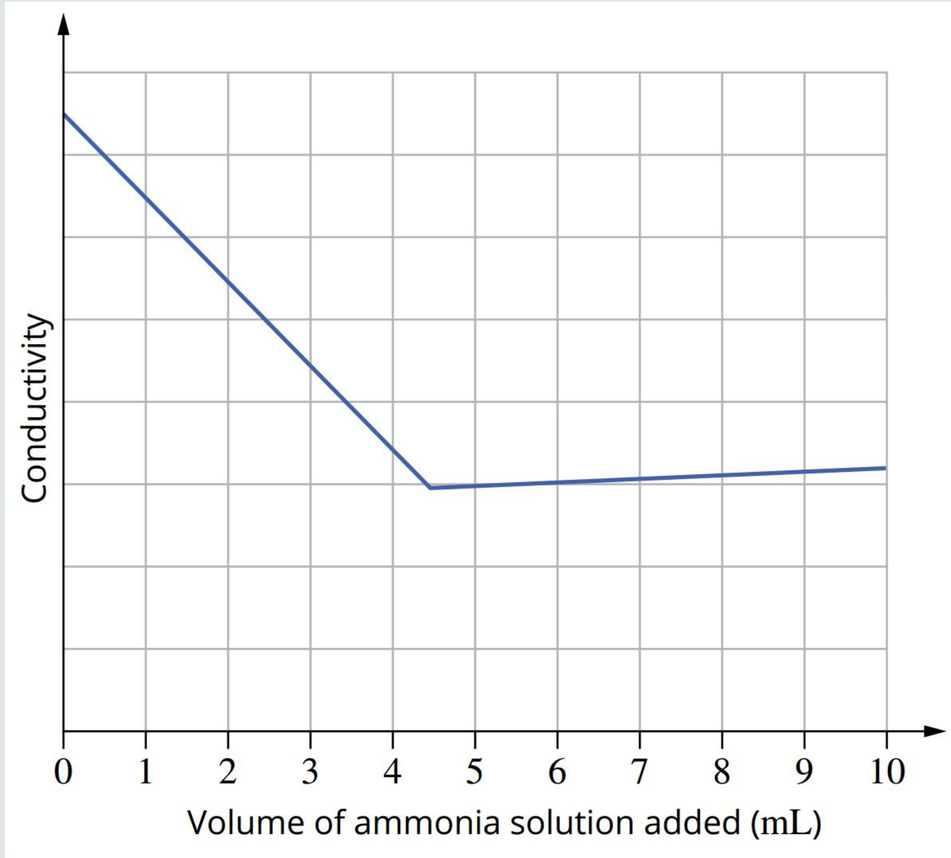
- **a** pipette
- **b** conical flask
- **c** burette

29 HA is a monoprotic acid, and MOH is a base. The titration curve shown below is obtained when 20.0 mL of 0.100 mol L^{-1} HA is titrated with MOH.



- **a** Determine if HA is a strong acid or a weak acid. Explain your reasoning.
- **b** Methyl orange changes colour in the pH range 3.1–4.4, while phenolphthalein changes colour in the pH range 8.3–10.0. Select the indicator that would be the most suitable to use for this titration. Explain your reasoning.
- **c** Determine the concentration, in mol L^{-1}, of the base, MOH.

30 An aqueous solution of ammonia is added to a solution containing hydrochloric acid. A graph of conductivity against volume of ammonia solution added is shown below.



The molar conductivity of some relevant ions is shown in Table 4.4.3 on page 128.

Explain the shape of the graph. Include two balanced equations in your answer.

Interpret

31 A manufacturer wants to know the exact concentration of hydrochloric acid in the concrete cleaner it produces.

- **a** What substance would you use to make a standard solution for this titration, and why have you chosen this substance?
- **b** Describe how you would prepare this standard solution for volumetric analysis.
- **c** Explain how each piece of glassware used in a titration should be rinsed to ensure you obtain accurate and precise results.
- **d** A 25.00 mL sample of the concrete cleaner was diluted to 250.0 mL in a volumetric flask. A 25.00 mL aliquot of 0.5000 mol L^{-1} potassium carbonate solution was placed in a conical flask. Methyl orange indicator was added, and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 18.45 mL of the diluted cleaner had been added. Calculate the concentration of hydrochloric acid in the concrete cleaner.
- **e** Determine whether the concentration calculated would be different if you used a standard solution of another base.

32 A chemistry student used the following method to determine the concentration of a dilute solution of butanoic acid (pK_a = 4.82). The student weighed out 1.500 g of solid NaOH on an electronic balance and then made up the solution in a 250.0 mL volumetric flask. The student then performed titrations, using bromocresol green as the indicator. This indicator is yellow below pH 3.2 and green above pH 5.2.
The titration results are shown in the table.

Titre	Volume of NaOH(aq) (mL)
1	16.35
2	10.10
3	12.35
4	11.25

Explain why this method produces inaccurate and unreliable results.

33 A student designed and performed an experiment to determine the ammonia content of a window-cleaning solution. In the experiment, a 25.00 mL aliquot of the cleaner was transferred to a 250.0 mL volumetric flask, and the volume was made up to the calibration line using deionised water. A 20.00 mL aliquot of this diluted cleaner solution required 24.35 mL of 0.195 mol L^{-1} hydrochloric acid to reach the end point.

- **a** Write a balanced equation for the reaction between ammonia and hydrochloric acid.
- **b** Using the student's data, calculate the concentration of ammonia in the 20.00 mL diluted cleaner aliquot.
- **c** Determine the concentration of ammonia in the window cleaner.
- **d** Use Table 4.3.1 on page 115 to identify a suitable indicator to use in this titration.
- **e** The calculated concentration of ammonia was considerably less than the value given on the label of the window cleaner. Which one or more of the following errors would account for the lower-than-expected calculated concentration? Justify your answers.
  - **i** The 20.00 mL pipette was rinsed only with deionised water prior to its use.
  - **ii** The burette was rinsed only with deionised water prior to its use.
  - **iii** The volumetric flask was rinsed only with water prior to its use.
  - **iv** Phenolphthalein indicator was used to determine the end point.

Data analysis

DATA SET 1

The information below applies to Questions 1–7.

The pH value of carbonated soft drinks typically ranges from 2.5 to 3.5. Citric acid, a weak triprotic acid, is one of the acids in carbonated soft drinks, acting as both a preservative and flavouring.

A student performed a titration to determine the concentration of citric acid in a popular soft drink. Part of the report presented by the student is shown below.

Part A: Standardisation of sodium hydroxide solution

1 Weigh approximately 5 g of the weak monoprotic acid potassium hydrogen phthalate (KHP) and transfer to a 100 mL volumetric flask. Add 100 mL of deionised water, stopper the flask and invert several times so that the solution is thoroughly mixed.

2 Place a 25 mL aliquot of the KHP standard solution into a conical flask. Add three drops of phenolphthalein indicator.

3 Titrate the KHP aliquot with the sodium hydroxide solution until the end point is reached.

4. Repeat the titration until three concordant titres are obtained.

Part B: Determination of citric acid concentration

1 Gently heat a 50 mL sample of the soft drink to remove CO_2. Allow to cool.

2 Transfer 30 mL of the cooled drink sample to a 100 mL volumetric flask and add deionised water up to the mark.

3 Place a 25 mL aliquot of the diluted soft drink solution into a conical flask. Add three drops of phenolphthalein indicator.

4 Titrate the standardised sodium hydroxide solution with the diluted soft drink aliquot until the end point is reached.

5 Repeat the titration until three concordant titres are obtained.

The experimental data collected by the student are shown in Table 1.

TABLE 1 Titration data

Part A: Standardisation of sodium hydroxide solution	
Molar mass of KHP = 204.23 g mol^{-1}	
Mass of KHP = 4.878 g	
Titration	Volume NaOH (mL)
1	27.60
2	26.50
3	26.45
4	26.55
Part B: Determination of citric acid concentration	
Average titre volume of NaOH(aq) = 12.90 mL	

Question 1 (2 marks)

Why does the sodium hydroxide solution need to be standardised by titration with KHP?

Question 2 (1 mark)

Identify the colour change at the end point for Part A.

Question 3 (5 marks)

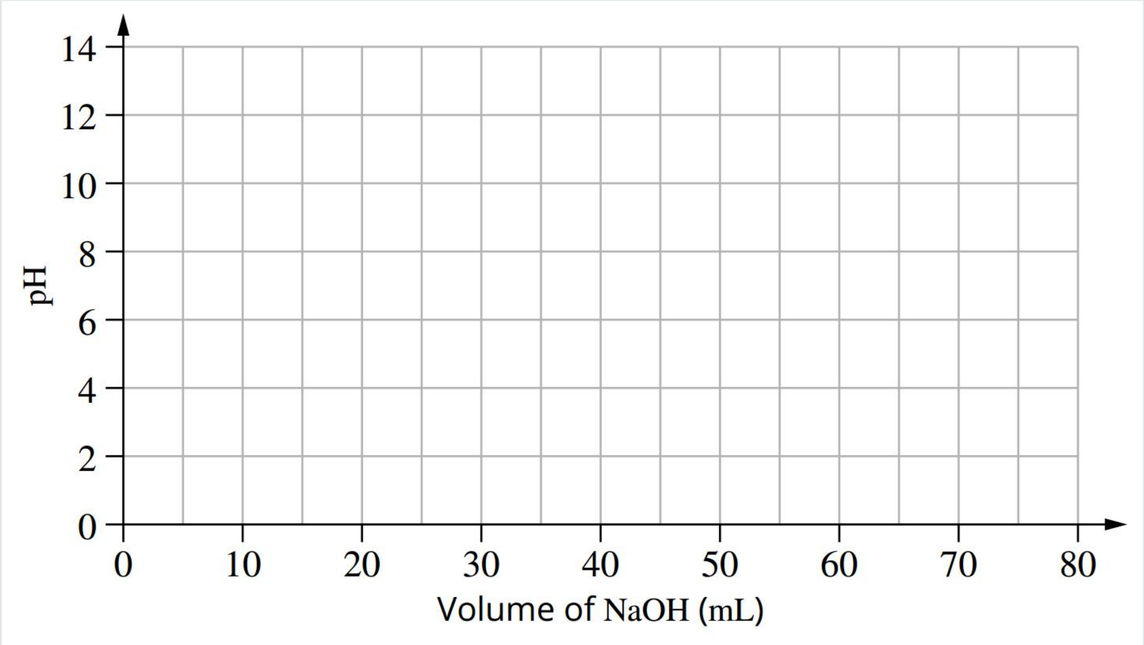
Using the student's data in Part A, calculate the concentration of the sodium hydroxide solution.

Question 4 (4 marks)

Using the student's data in Part B and the sodium hydroxide concentration calculated in question **3**, determine the concentration of the citric acid in the soft drink.

Question 5 (4 marks)

On the grid below, sketch the expected pH curve for the titration in Part A between the KHP standard solution and the sodium hydroxide solution. Label the half-equivalence point and the equivalence point.



Question 6 (2 marks)

Explain how your answer to question **5** would be different if the carbon dioxide was not removed from the soft drink.

Question 7 (2 marks)

Identify one mistake in the student's procedure. Explain how the procedure should be changed to eliminate this mistake.

CHAPTER 05

Redox reactions

Some of the most important chemical reactions for sustaining life, for energy production and storage, and for maintaining the delicate balance of our oceans and atmosphere are classified as redox reactions.

In this chapter, you will learn how redox reactions can be defined in terms of electron transfer, and how this definition can be extended by using the concept of oxidation number. You will construct balanced half-equations that describe the transfer of electrons, and then combine these half-equations to create an overall equation for the reaction. You will also learn about the practical implications of redox reactions involving metals, including consideration of the reactivity series of metals, metal displacement reactions, combustion reactions, and the corrosion of metals.

Syllabus subject matter

Topic 2 • Oxidation and reduction

REDOX REACTIONS

- Identify that displacement reactions of metals, combustion, corrosion and electrochemical processes can be modelled as redox reactions involving oxidation of one substance and reduction of another substance. **5.1, 5.2, 5.3**
- Determine the species that are oxidised and reduced, and the oxidising agent and reducing agent, in redox reactions. **5.1, 5.2, 5.3**
- Explain that oxidation can be modelled as the loss of electrons from a chemical species, and reduction can be modelled as the gain of electrons by a chemical species; these processes can be represented using balanced half-equations and redox equations (acidic conditions only). **5.1, 5.2, 5.3**
- Determine the oxidation state (represented with the sign given before the number) of an atom in an ion or compound, e.g. +2. **5.2**
- Apply oxidation numbers (represented as roman numerals) to name transition metal compounds. **5.2**
- Apply half-equations and oxidation numbers to balance redox equations (acidic conditions only) and to discriminate between the species that are oxidised and reduced, and the oxidising agent and reducing agent. **5.1, 5.2, 5.3**
- Analyse data, including displacement reactions of metals, combustion, corrosion and electrochemical processes, to determine redox reactions. **5.1**

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5.1 Introducing redox reactions

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- describe redox reactions in terms of electron transfer
- recall that oxidation involves loss of electrons and reduction involves gain of electrons
- represent simple redox reactions using half-equations
- determine the oxidising and reducing agents in simple redox reactions
- understand the reactivity of metals and metal displacement reactions in terms of redox processes
- understand the causes and effects of corrosion in terms of redox processes.

FIGURE 5.1.1 Potassium burning in chlorine gas—a spectacular example of a redox reaction

Your everyday life depends on a large number of chemical reactions. Many of these are **redox reactions**. The term 'redox' is derived from the specific reduction and oxidation processes that, when combined, complete the overall redox reaction.

Redox reactions are occurring within you and around you all the time. From the respiration reactions that enable the cells of your body to produce energy, and the combustion reactions that warm your home, to the reactions in the batteries that keep your mobile phone working. The spectacular reaction between potassium and chlorine gas shown in Figure 5.1.1 is also an example of a redox reaction.

REDOX REACTIONS—ELECTRON TRANSFER REACTIONS

Fundamentally, redox reactions involve a transfer of electrons from one chemical species to another. The atom, molecule or ion that loses electrons during a redox reaction is said to have undergone **oxidation**—oxidation involves loss of electrons. The atom, molecule or ion that gains electrons during a redox reaction is said to have undergone **reduction**—reduction involves gain of electrons.

Early understandings of redox reactions

When chemistry evolved from the ancient study of alchemy, many of the reactions known to early chemists involved air. French chemist Antoine Lavoisier identified the reactive component of air and named it oxygen. As a result, reactions in which oxygen was a reactant were described as oxidation reactions. In air, the combustion of an element such as carbon, sulfur or iron produces an oxide:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
$$S(s) + O_2(g) \rightarrow SO_2(g)$$
$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Because elemental iron reacts readily with oxygen, iron is found in nature in ores containing minerals, such as haematite (Fe_2O_3) and magnetite (Fe_3O_4). The iron metal used extensively for construction has been extracted from iron ore in a blast furnace.

The extraction of iron from iron ore in a blast furnace can be represented by the equation:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

In this reaction, the iron(III) oxide has lost oxygen and the carbon monoxide has gained oxygen. The iron(III) oxide is described as having been **reduced** and the carbon monoxide is described as having been **oxidised**.

Origins of the words 'oxidation' and 'reduction'

Scientists first used the term 'oxidation' in the late 18th century after the work of Antoine Lavoisier. Lavoisier showed that the 'burning' of metals, such as mercury, involved a combination with oxygen.

The term 'reduction' was used long before this to describe the process of extracting metals from their ores. The word 'reduction' comes from the Latin *reduco*, meaning to restore.

The process of metal extraction was seen as restoring the metal from its compounds, such as iron from iron oxide or copper from copper(II) oxide. The reduction of copper(II) oxide to form copper powder occurs when copper(II) oxide is heated in the presence of hydrogen or methane gas, as shown in Figure 5.1.2. Some fine particles of copper escape with the gas, causing the green flame.

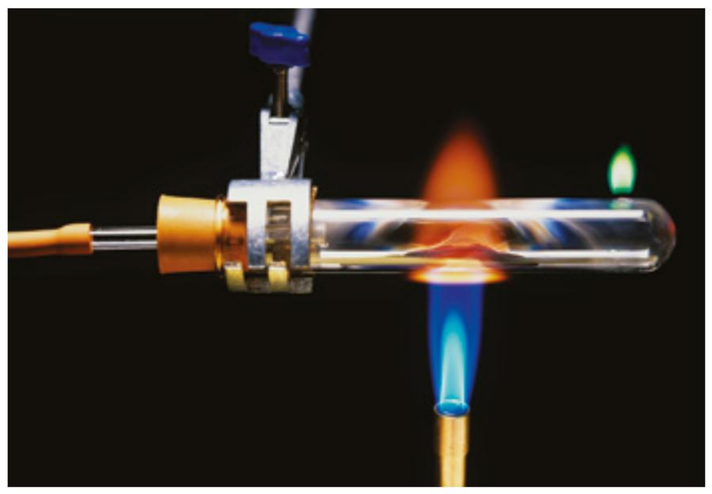


FIGURE 5.1.2 The reduction of copper(II) oxide to form copper powder occurs when it is heated in the presence of hydrogen or methane gas.

Transfer of electrons

Figure 5.1.3 shows that when a piece of magnesium ribbon is heated in a flame, it burns with a brilliant white flame. Magnesium oxide powder is the product formed from this chemical reaction.

FIGURE 5.1.3 Magnesium ribbon burns brightly when heated in air to form a white powder, magnesium oxide.

This reaction can be represented by the equation:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

The reaction involves a loss and gain of electrons by the reactants, which can be represented by two **half-equations**.

Each magnesium atom loses two electrons to form a magnesium (Mg^{2+}) ion. The half-equation for this part of the overall reaction is written as shown. The condensed electron configurations are also shown:

$$Mg(s) \rightarrow Mg^{2+}(s) + 2e^-$$
$$[Ne]3s^2 \quad [He]2s^22p^6$$

Notice that when electrons are lost, they appear as products (on the right-hand side) in the half-equation.

At the same time, each oxygen atom in the oxygen molecule (O_2) gains two electrons (i.e. four electrons per oxygen molecule):

$$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$$
$$[He]2s^22p^4 \quad [He]2s^22p^6$$

Notice that when electrons are gained, they appear as reactants (on the left-hand side) in the half-equation. The electrons that are gained by the oxygen have come from the magnesium atoms.

Note that there is no overall loss of electrons, but a transfer of electrons from one atom to another. If an atom, ion or molecule loses electrons, there must be another atom, ion or molecule that gains electrons. Therefore, oxidation and reduction always occur simultaneously and cannot occur independently of one another.

Atoms also lose and gain electrons in many other reactions, and this transfer of electrons provides a widely used definition of oxidation and reduction.

The simple mnemonic 'OIL RIG' can be used to assist in remembering the differences between oxidation and reduction processes:

Oxidation
Is
Loss
Reduction
Is
Gain

Oxidation is defined as the loss of electrons. Reduction is defined as the gain of electrons.

Electron transfer, electron configurations and the periodic table

The burning of magnesium described above involves metal magnesium atoms losing electrons and non-metal oxygen atoms gaining electrons. You may recall from Units 1 and 2 that metals have relatively low electronegativity values and ionisation energies. This means that metal atoms have a relatively low tendency to draw valence electrons to themselves in chemical bonds and tend to lose valence electrons to other species in chemical reactions. In other words, metals tend to undergo oxidation during chemical reactions. Conversely, non-metals have relatively high electronegativity and electron affinity values. This means that non-metal atoms have a strong tendency to draw valence electrons to themselves in chemical bonds and tend to gain valence electrons from other species in chemical reactions. In other words, non-metals tend to undergo reduction during chemical reactions.

When a metal atom loses electrons, the atom becomes a stable cation with a stable electron configuration. In the case of the magnesium atom, there are 12 electrons in total, with two electrons in the valence shell. The condensed electron configuration is [Ne]$3s^2$. The loss of the two valence electrons leads to the formation of the Mg^{2+} ion, which has an electron configuration equivalent to that of the noble gas, neon (i.e. [He]$2s^2 2p^6$)—which you know has a very stable electron configuration.

When a non-metal atom gains electrons, the atom becomes a stable anion with a stable electron configuration. In the case of the oxygen atom, there are eight electrons in total, with six electrons in the valence shell. The condensed electron configuration is [He]$2s^2 2p^4$ and the valence shell can readily accommodate (or accept) two more electrons. The gain of two valence electrons forms the oxide ion, O^{2-}, which also has the same stable electron configuration as neon (i.e. [He]$2s^2 2p^6$).

When atoms undergo redox processes, the number of electrons transferred is determined by the electron configurations of the atoms involved. Electrons are lost or gained to achieve a stable electron configuration. For main group elements, this means that the position of the element in the periodic table can be used to predict how many electrons will be lost or gained.

Figure 5.1.4 shows the stable ions for a range of main group elements. You can see that a **main group metal** loses enough electrons to achieve the same number and arrangement of electrons as the noble gas immediately preceding it in the periodic table. Conversely, a main group non-metal gains enough electrons to achieve the same number and arrangement of electrons as the noble gas immediately following it in the periodic table.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Li^+														N^{3-}	O^{2-}	F^-	Noble gases
Na^+	Mg^{2+}											Al^{3+}			S^{2-}	Cl^-	
K^+	Ca^{2+}											Ga^{3+}			Se^{2-}	Br^-	
Rb^+	Sr^{2+}														Te^{2-}	I^-	
Cs^+	Ba^{2+}																

FIGURE 5.1.4 Predicting ionic charges using the periodic table

Other examples of redox reactions

Many redox reactions do not involve a reaction with oxygen. The reaction between potassium and chlorine shown in Figure 5.1.1 on page 146 is an example:

$$2K(s) + Cl_2(g) \rightarrow 2KCl(s)$$

Oxidation half-equation: $K(s) \rightarrow K^+(s) + e^-$

Reduction half-equation: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$

Another example is the reaction between copper and liquid sulfur:

$$Cu(s) + S(l) \rightarrow CuS(s)$$

Oxidation half-equation: $Cu(s) \rightarrow Cu^{2+}(s) + 2e^-$

Reduction half-equation: $S(l) + 2e^- \rightarrow S^{2-}(s)$

You will note that in each of the above chemical equations the charge on each of the atoms changes during the chemical reaction. A change in electrical charge on atoms, ions or molecules is one way that chemical reactions can be identified as redox reactions.

Worked example 5.1.1

UNDERSTANDING SIMPLE OXIDATION AND REDUCTION REACTIONS

Construct the oxidation and reduction half-equations for the reaction with the overall equation:

$$2Li(s) + Br_2(l) \rightarrow 2LiBr(s)$$

Thinking	Working
Identify the ions in the product.	LiBr is made up of Li^+ and Br^- ions.
Construct the half-equation for the oxidation of the reactant that forms positive ions and balance the equation with electrons.	$Li(s) \rightarrow Li^+(s) + e^-$
Construct the half-equation for the reduction of the reactant that forms negative ions and balance the equation with electrons.	$Br_2(l) + 2e^- \rightarrow 2Br^-(s)$

➤ Try yourself 5.1.1

UNDERSTANDING SIMPLE OXIDATION AND REDUCTION REACTIONS

Construct the oxidation and reduction half-equations for the reaction with the overall equation:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

Oxidising agents and reducing agents

Just as an employment agent enables a client to become employed, an **oxidising agent**, or **oxidant**, enables or causes another chemical to be oxidised. Similarly, a **reducing agent**, or **reductant**, enables or causes another chemical to be reduced. Redox reactions always involve an oxidising agent and a reducing agent that react together.

In the reaction between magnesium and oxygen shown in Figure 5.1.5, magnesium is being oxidised by oxygen. So, oxygen is the oxidising agent. In turn, oxygen is gaining electrons from magnesium. It is being reduced by magnesium, so magnesium is the reducing agent.

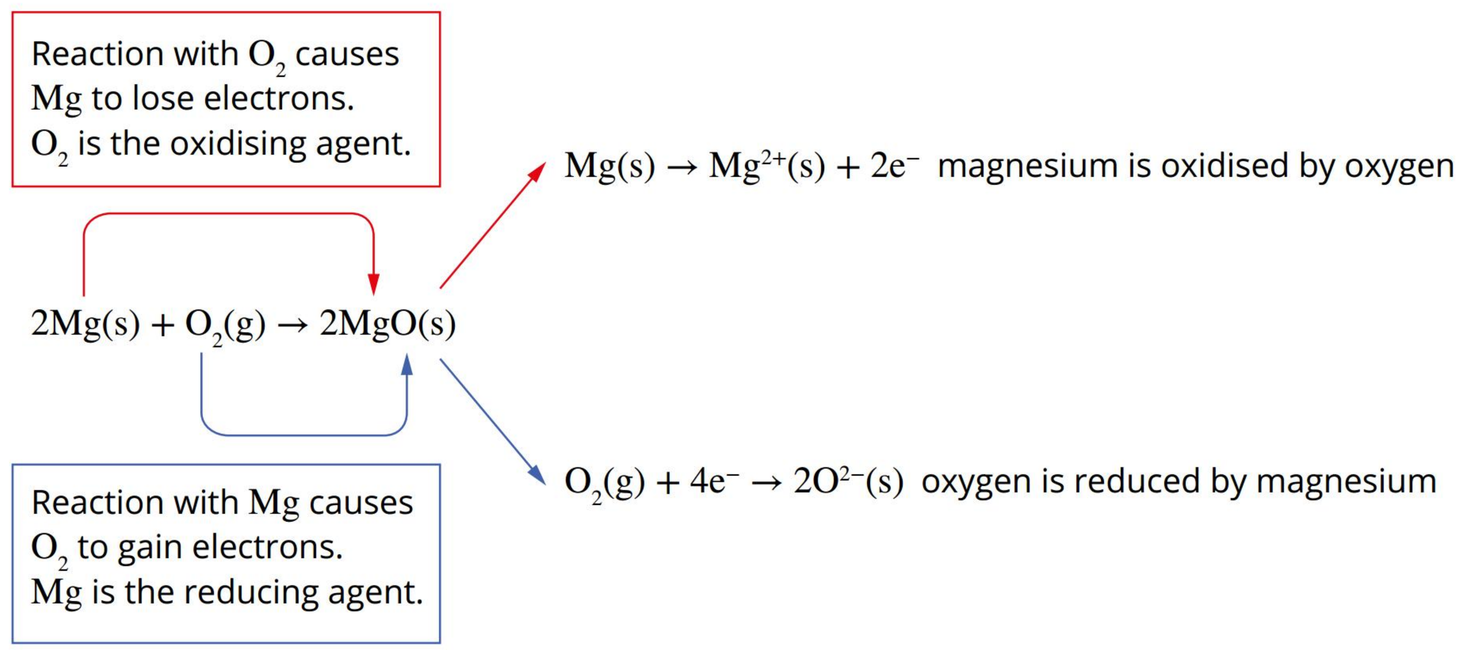


FIGURE 5.1.5 In the reaction between magnesium and oxygen, magnesium is the reducing agent and oxygen is the oxidising agent.

Since metals tend to lose electrons, they act as reducing agents. Conversely, since non-metals tend to gain electrons, they act as oxidising agents.

Figure 5.1.6 summarises the list of redox terms introduced in this module.

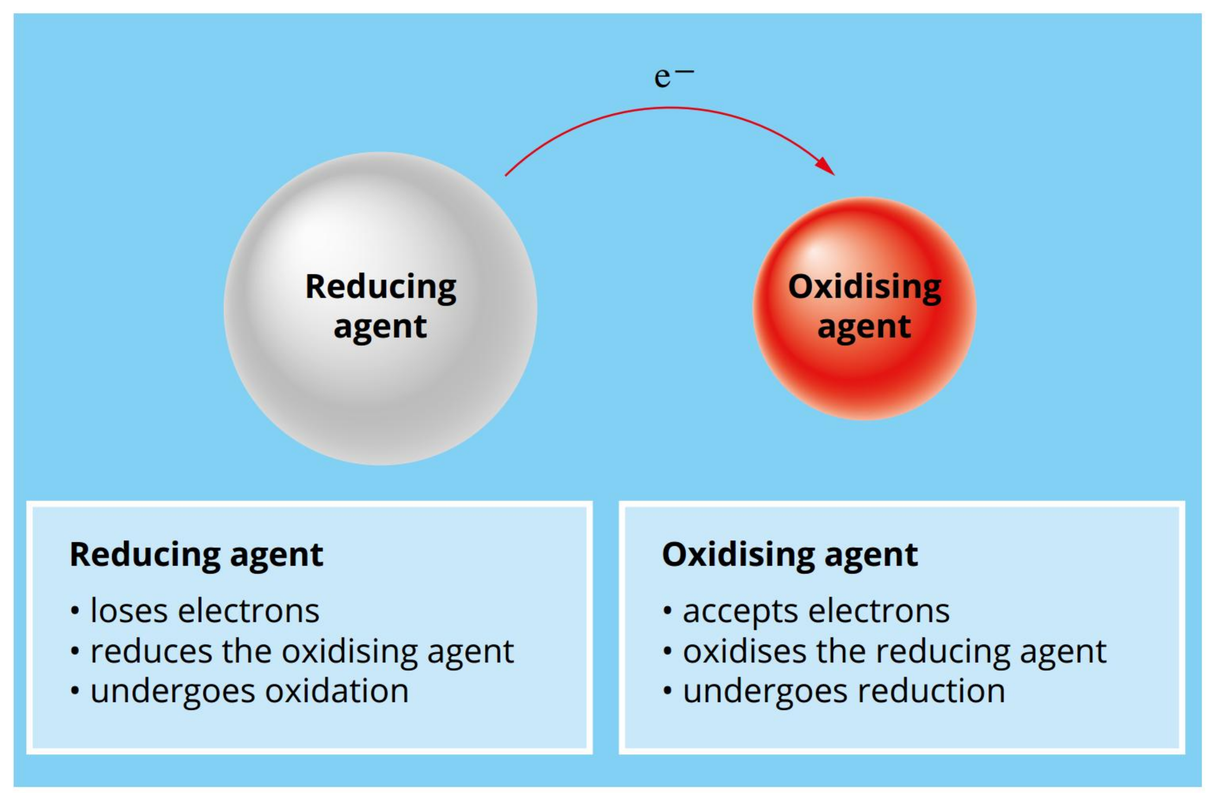


FIGURE 5.1.6 Summary of redox reaction terms

Reducing agents cause another chemical to be reduced. In the reaction, they are oxidised.

Oxidising agents cause another chemical to be oxidised. In the reaction, they are reduced.

Balancing simple redox equations

Half-equations enable you to see the details of what is happening in a redox reaction. Like other chemical equations, half-equations must be balanced so there is the same number of atoms of each element on each side of the arrow. Similarly, charge must also be balanced. Half-equations and full redox equations should indicate the states of all the species in the reaction as well.

Worked example 5.1.2

WRITING SIMPLE HALF-EQUATIONS

When sodium metal reacts with fluorine gas (F_2), solid sodium fluoride is formed. The oxidation and reduction reactions can be represented by two half-equations.

Construct these half-equations and identify the substances that are oxidised and reduced.

Thinking	Working
Identify one reactant and the product it forms and represent them on each side of an equation. Balance the equation for the element.	$F_2(g) \rightarrow 2F^-(s)$
Add electrons to balance the equation for charge.	$F_2(g) + 2e^- \rightarrow 2F^-(s)$
To decide whether the reactant is oxidised or reduced, remember that oxidation is loss of electrons and reduction is gain of electrons.	Electrons are gained, so this is reduction. $F_2(g)$ is being reduced.
Identify the second reactant and the product it forms and represent them on each side of an equation. Balance the equation for the element.	$Na(s) \rightarrow Na^+(s)$
Add electrons to balance the equation for charge.	$Na(s) \rightarrow Na^+(s) + e^-$
To decide whether the reactant is oxidised or reduced, remember that oxidation is loss of electrons and reduction is gain of electrons.	Electrons are lost, so this is oxidation. Na(s) is being oxidised.

➤ Try yourself 5.1.2

WRITING SIMPLE HALF-EQUATIONS

When a piece of copper metal is placed into a silver nitrate solution, silver metal is formed and the solution gradually turns blue, indicating the presence of copper(II) ions in the solution. The oxidation and reduction reactions can be represented by two half-equations.

Construct these half-equations and identify the substances that are oxidised and reduced.

Writing an overall redox equation

When writing equations for redox reactions, the two half-equations are normally written first and then added together to obtain an overall equation.

An overall equation does not show any electrons transferred; all the electrons lost in the oxidation reaction are gained in the reduction reaction. One, or perhaps both, of the half-equations may need to be multiplied by a factor to ensure that the electrons balance and can be cancelled out in the overall equation.

Consider the reaction of sodium and chlorine gas. In this reaction, each Na atom is oxidised and loses one electron. Each Cl_2 molecule is reduced and gains two electrons:

$$Na(s) \rightarrow Na^+(s) + e^-$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$

Two Na atoms must therefore be oxidised to provide the electrons required for each chlorine molecule to be reduced. To write an overall equation for this reaction, the half-equation involving the oxidation of Na is multiplied by a factor of two before combining it with the half-equation for reduction of Cl_2:

$$2Na(s) \rightarrow 2Na^+(s) + 2e^-$$

You can now write the two half-equations and add them to find the overall equation:

$$2Na(s) \rightarrow 2Na^+(s) + 2e^-$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$

When the electrons have been cancelled, the overall equation is:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

When writing an overall redox equation from two half-equations, you need to balance the number of electrons.

Worked example 5.1.3

BALANCING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Sodium metal is oxidised by oxygen gas in air to form solid sodium oxide.

Construct the half-equations for the reaction and hence construct the balanced overall equation.

Thinking	Working
Identify one reactant and the product it forms and represent them on each side of the equation. Balance the equation for the element.	$O_2(g) \rightarrow 2O^{2-}(s)$
Add electrons to balance the equation for charge.	$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$
Identify the second reactant and the product it forms and represent them on each side of the equation. Balance the equation for the element.	$Na(s) \rightarrow Na^+(s)$
Add electrons to balance the equation for charge.	$Na(s) \rightarrow Na^+(s) + e^-$
Multiply one equation by a suitable factor to ensure that the number of electrons is balanced. In this case, you multiply the oxidation half-equation by 4 since the reduction of oxygen requires four electrons, so the oxidation of sodium must supply four electrons.	$(Na(s) \rightarrow Na^+(s) + e^-) \times 4$ $4Na(s) \rightarrow 4Na^+(s) + 4e^-$
Add the oxidation and reduction half-equations together, cancelling out electrons so that none are in the final equation. Combine ions to create the formula of the product.	$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$ $4Na(s) \rightarrow 4Na^+(s) + 4e^-$ When the electrons have been cancelled, the overall equation is: $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

➤ Try yourself 5.1.3

BALANCING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Aluminium metal is oxidised by oxygen gas in air to form solid aluminium oxide.

Construct the half-equations for the reaction and hence construct the balanced overall equation.

THE REACTIVITY SERIES OF METALS

Some metals react quickly and vigorously with oxygen and water, and even more vigorously with acids. The reaction between other metals with oxygen is quite slow. Silver cutlery oxidises slowly in the air, producing a black silver oxide coating, while the reaction of magnesium ribbon in acid is more vigorous. These are both examples of redox reactions.

Reactivity of metals

Sodium, magnesium and iron are metals that are relatively easily oxidised. Sodium is oxidised so easily that it has to be stored under paraffin oil to prevent it from reacting with oxygen in the atmosphere. The oxidation of iron, which can eventually result in the formation of rust, can be an expensive problem.

Other metals do not oxidise as readily. For example, platinum and gold are sufficiently inert and are found as pure elements in nature.

Figure 5.1.7 shows a comparison of four different metals reacting with dilute acid. By observing how readily metals react with oxygen, water, dilute acids and other metal salts, it is possible to determine an order of reactivity of metals.

The metals can be ranked in a list according to their reactivity, or ability to act as reducing agents. Figure 5.1.8 shows such a ranking, which is also known as a **reactivity series of metals**. Figure 5.1.9 shows the half-equations written from left to right as reduction reactions for the metal cations as each cation gains electrons to form the corresponding metal. These reactions are reversible, so a two-way arrow is written to indicate this.

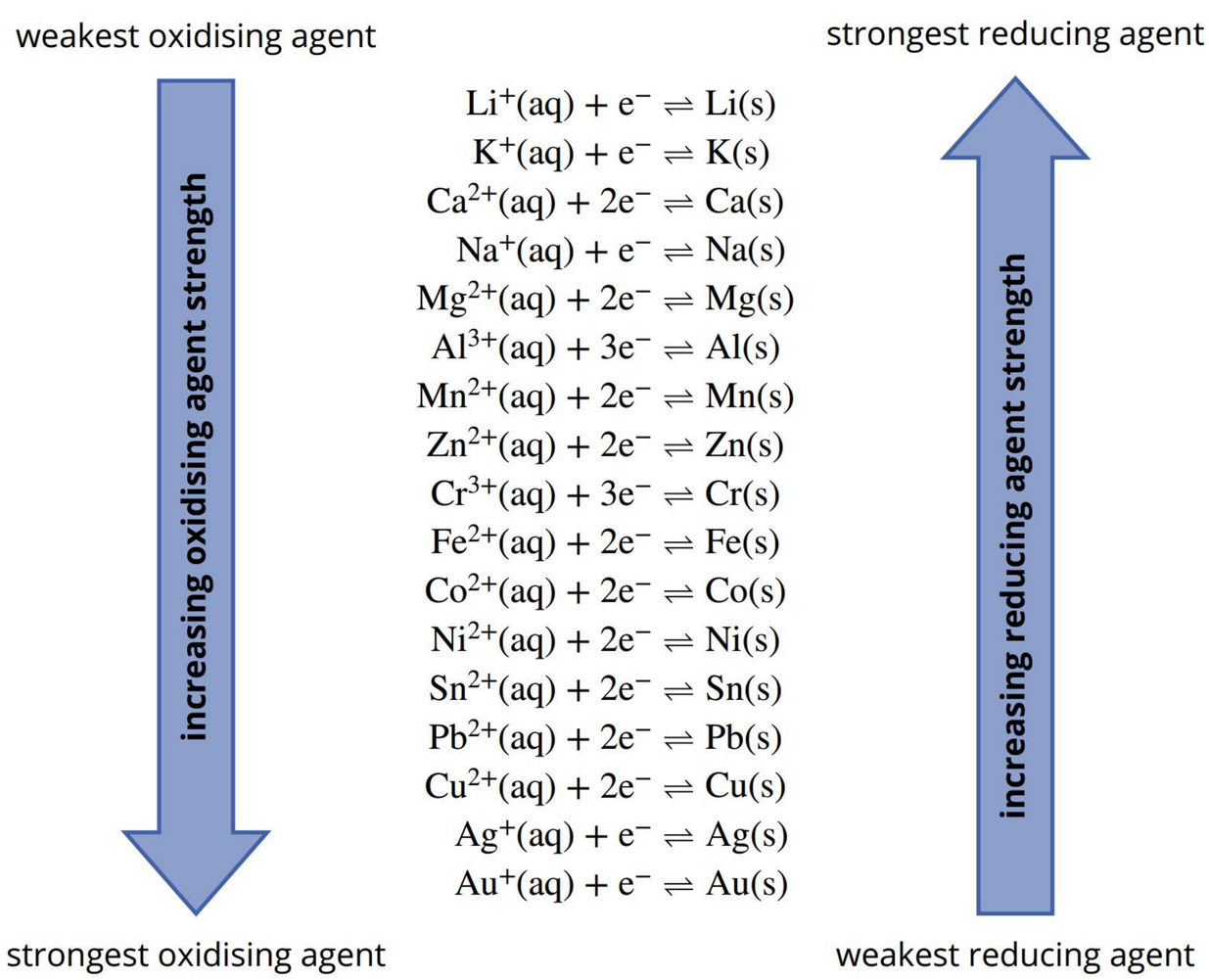


FIGURE 5.1.9 Reversible redox equations representing the redox reactions between metals (oxidising agents) and their ions (reducing agents), listed in order from the strongest reducing agent (at the top) to the weakest reducing agent (at the bottom).

In general, metals listed higher in the metal reactivity series shown in Figure 5.1.8 tend to be more readily oxidised (lose electrons) than those listed lower down in the table. They tend to be stronger reducing agents than those below them. This is reflected in Figure 5.1.9, which shows the relevant oxidation and reduction half-equations for metals and their corresponding cations. These half-equations are written as reduction reactions (from left to right) but are reversible as indicated by the double arrows. The metals on the right-hand side of Figure 5.1.9 are listed from the strongest reducing agent, Li(s), to the weakest, Au(s). You will note that the order of metals listed in Figures 5.1.8 and 5.1.9 are very similar, with minor variations being the result of differences in how chemical reactivity is measured compared to measurements of oxidising and reducing strengths.

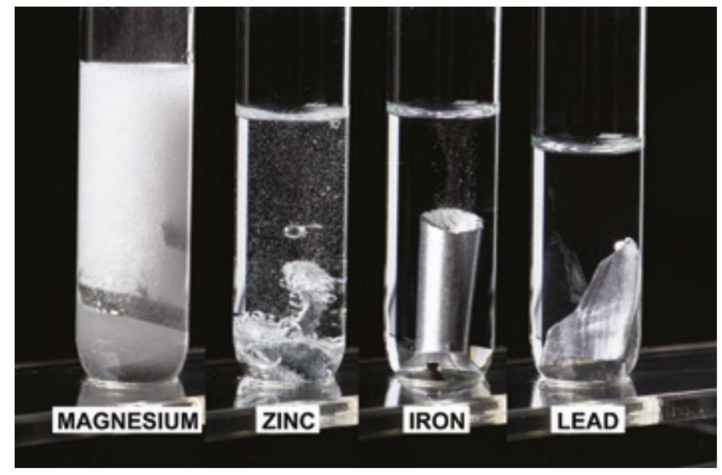


FIGURE 5.1.7 Some metals react with dilute acid to form a salt and hydrogen gas. The reaction between magnesium and dilute acid is extremely vigorous. The reaction between zinc and dilute acid is less vigorous. The reaction between iron and dilute acid is very slow. There is no reaction between lead and dilute acid. Based on this information, the order of metal reactivity from most reactive to least reactive is magnesium, zinc, iron and lead.

Element	Reactivity
K	most reactive
Na	
Li	
Ba	
Sr	
Ca	
Mg	
Al	
C*	
Mn	
Zn	
Cr	
Fe	
Cd	
Co	
Ni	
Sn	
Pb	
H_2*	
Sb	
Bi	
Cu	
Hg	
Ag	
Au	
Pt	least reactive

* Carbon (C) and hydrogen gas (H_2) added for comparison

FIGURE 5.1.8 Reactivity series of metals

As you go down the list of metals in Figure 5.1.9, the:

- metals, which are on the right-hand side, become less reactive. This means that the metals higher in the series are easier to oxidise and are therefore stronger reducing agents
- metal cations, which are on the left-hand side, become increasingly easier to reduce and therefore are more reactive. Cations lower in the series have a greater attraction for electrons, so they are easier to reduce and are therefore relatively strong oxidising agents.

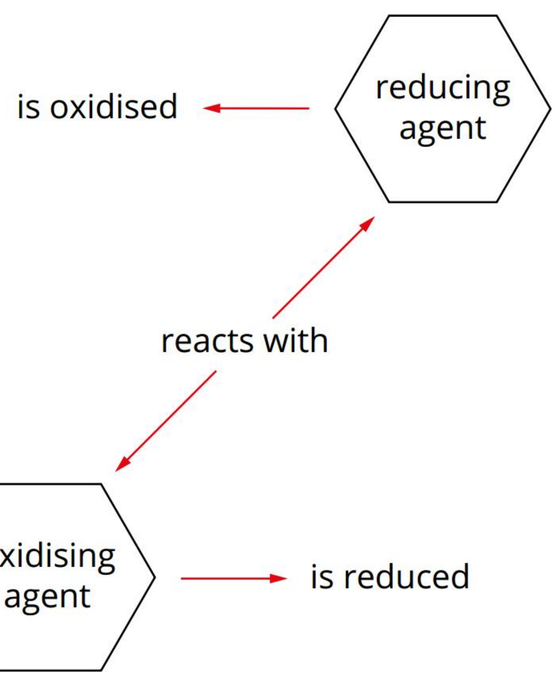


FIGURE 5.1.10 Predicting the reaction between an oxidising agent and a reducing agent

A metal ion lower in the reactivity series (an oxidising agent) will react with a metal higher in the reactivity series (a reducing agent).

Metal displacement reactions

The order in which metals and their metal ions appear in the reactivity series enables you to predict which metals will **displace** other metals from solutions of their ions. Such reactions are known as **metal displacement reactions**.

A more reactive metal will be oxidised by, and donate its electrons to, the cation of a less reactive metal. The cation receives the electrons and is reduced. In other words, for a naturally occurring **spontaneous redox reaction** to occur, the metal ions of one metal must be below the other metal in the reactivity series, as shown in Figure 5.1.10. The more reactive metal acts as the reducing agent, and the metal ions of the other metal act as the oxidising agent.

When a strip of copper wire is placed in a solution of silver nitrate, as shown in Figure 5.1.11, silver ions are reduced to silver atoms by copper atoms. The silver atoms are deposited as silver crystals. The copper atoms are oxidised to form a blue solution containing copper(II) ions. As a result of the reaction, copper(II) ions have displaced silver ions from the solution.

Silver ions have oxidised copper atoms, consistent with their order in the reactivity series, as shown in Figure 5.1.12. The overall redox reaction can be represented by the equation:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

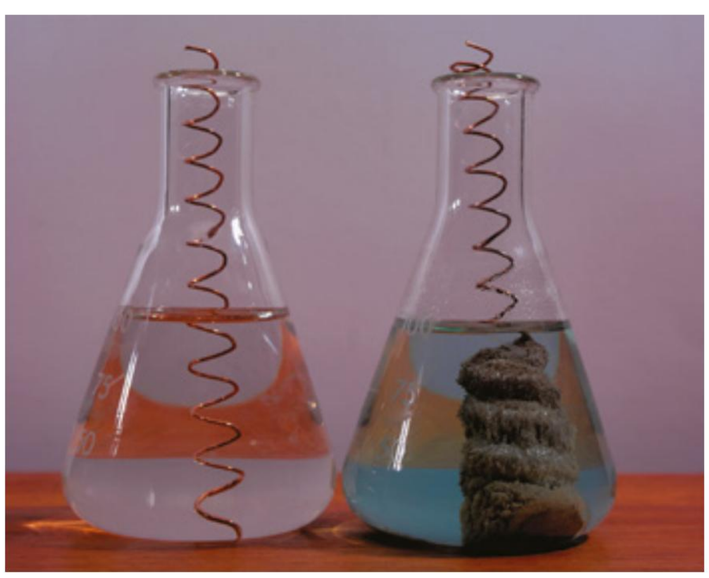


FIGURE 5.1.11 When a strip of copper wire is suspended in a solution of silver nitrate in the flask on the left, long crystals of silver metal start to form. In the flask on the right, the copper has displaced the silver from the solution.

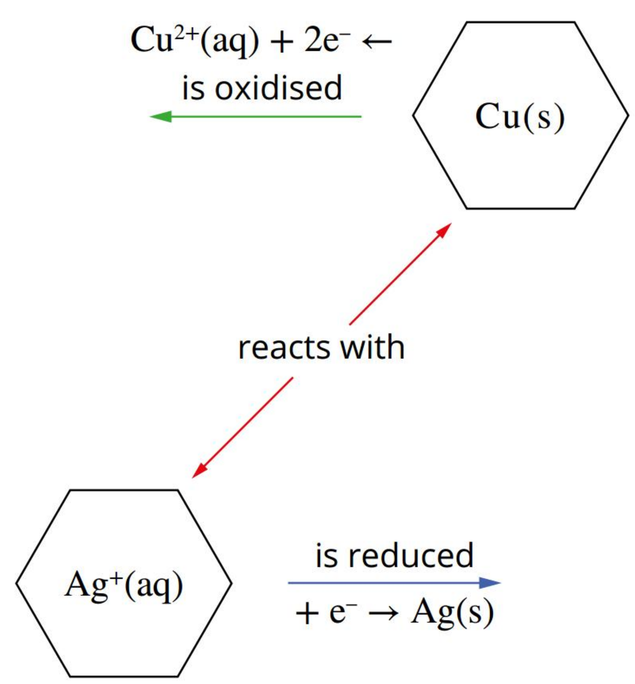


FIGURE 5.1.12 A spontaneous redox reaction occurs when copper is added to a solution of silver nitrate. Silver ions oxidise copper atoms.

According to the reactivity series, a metal displacement reaction is predicted to occur when zinc is added to copper(II) sulfate solution, as shown in Figure 5.1.13. The technique for making this prediction is shown in Worked example 5.1.4.

Worked example 5.1.4

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether zinc will displace copper from a solution containing copper(II) ions and, if appropriate, construct the overall equation for the reaction.

Thinking	Working
Locate the metal and the metal ion in the list of redox equations shown in Figure 5.1.9 on page 153.	Metals (reducing agents) are on the right-hand side of Figure 5.1.9 and metal ions (oxidising agents) are on the left-hand side. $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$ $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ $Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$ $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$ $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$ $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
Determine whether the metal is higher in the list of redox equations shown in Figure 5.1.9 than the metal cation. If this is the case, there will be a reaction.	Zn(s) is on the right-hand side because it is a reducing agent and it is above $Cu^{2+}(aq)$, so there will be a reaction.
Write the reduction half-equation for the metal ion directly as it is written in Figure 5.1.9, including states and using a one-way arrow.	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Write the oxidation half-equation for the metal, writing the metal on the left-hand side of the arrow (as a reactant). Include states and use a one-way arrow.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
Combine the two half-equations, balancing electrons, to give the overall equation for the reaction.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
Answer the original question, predicting whether the reaction will occur.	This equation confirms that zinc will displace copper from a solution containing copper(II) ions.

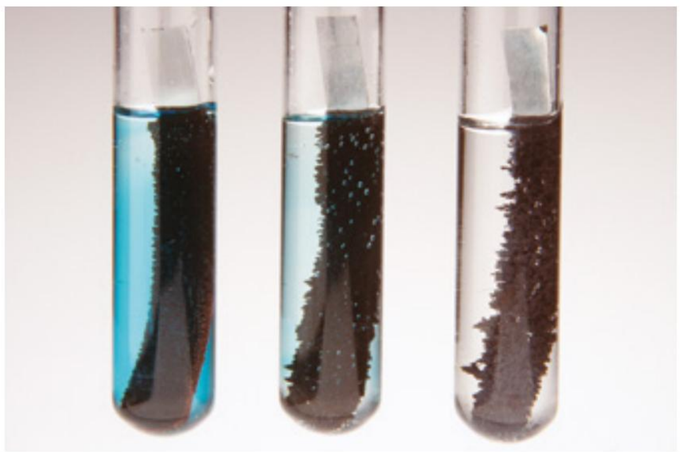


FIGURE 5.1.13 A brown deposit of copper metal is observed forming on the zinc, and the blue copper(II) sulfate solution gradually becomes colourless as the concentration of Cu^{2+} ions decreases.

➤ Try yourself 5.1.4

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether tin will displace silver from a solution containing silver ions and, if appropriate, construct the overall equation for the reaction.

CORROSION

The reactions that occur when metals corrode are redox reactions. The costs associated with corroding metals are substantial, especially because iron, which is particularly prone to corrosion in the presence of water and oxygen, is so widely used as a structural material for buildings, bridges, gas and water pipes, and ships. The effect of corrosion in water pipes is evident in the pumping system shown in Figure 5.1.14.

FIGURE 5.1.14 Corrosion is causing water to leak from these pipes in a pumping system.

In Australia, about $50 billion (approximately 3% of gross domestic product) is spent each year in an effort to prevent metals from corroding and replacing metal that has corroded. Despite such efforts, steel structures continue to corrode, eventually producing the familiar orange-brown flakes known as rust, although corrosion prevention methods can slow down the rate of corrosion considerably.

This module will give you an opportunity to consider corrosion in terms of the causes and effects of an issue that relates to redox chemistry. In doing so, you will look at the redox reactions involved in corrosion both in the presence of water and in the absence of water.

Dry corrosion

Direct reaction with oxygen in the air to form a metal oxide is known as **direct corrosion** or **dry corrosion**. Sodium is so reactive that it must be stored under oil to prevent contact with oxygen. The following equation represents the dry corrosion of sodium:

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

Dry corrosion of aluminium forms a tough, impervious coating of aluminium oxide (Al_2O_3), which protects the metal underneath from further contact with oxygen. The aluminium window frame in Figure 5.1.15 is lightweight and resistant to corrosion. Therefore, it is an excellent material in situations where maintenance would be difficult.

FIGURE 5.1.15 An aluminium window frame is resistant to corrosion and is a useful material in situations where maintenance would be difficult.

Iron is much less reactive than sodium or aluminium; the rate of dry corrosion of iron is slow at room temperatures. When iron does corrode, it forms a coating that flakes off readily, leaving the metal underneath exposed to further corrosion.

Wet corrosion

The presence of moisture accelerates the corrosion of iron. This process is known as **wet corrosion**. The best-known example of wet corrosion is the formation of rust as a flaky, brown-red coating on iron.

Wet corrosion can occur in moist air or by direct immersion in water. Several factors affect the rate at which wet corrosion occurs. Consider the observations represented in Figure 5.1.16.

FIGURE 5.1.16 Wet corrosion. (a) A piece of steel wool (iron) does not corrode on supermarket shelves. However, once it becomes wet through use, it corrodes quickly. (b) An iron barbecue grill that has been coated with grease shows little sign of corrosion, even after being exposed to the rain for some time. (c) Rust in a car generally starts inside door frames, under mudguards, or in places where the paint has been chipped. (d) Shipwrecks corrode rapidly and will eventually disintegrate. (e) Corrosion occurs more rapidly in cities with a pollution problem, particularly where the pollutants include acidic oxides such as nitrogen dioxide and sulfur dioxide.

Each of these observations provides information about the factors that influence the rate of wet corrosion of iron. In general, corrosion is accelerated by:

- the presence of water
- impurities such as salt and acidic pollutants that dissolve in the water.

However, corrosion can be reduced when the iron is alloyed with certain other materials or when it has a protective coating.

The wet corrosion process

Rust is a hydrated oxide of iron with the formula $Fe_2O_3 \cdot xH_2O$. There can be 1–3 water molecules associated with the iron oxide in its structure. An understanding of the steps involved in corrosion helps scientists to identify methods of corrosion prevention.

Step 1: Iron is oxidised to form Fe^{2+} ions in one region on the iron surface:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

At the same time, in another region on the surface, using the electrons produced by the oxidation process, oxygen is reduced in the presence of water to hydroxide ions:

$$O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

The overall equation for step 1 is:

$$2Fe(s) + O_2(aq) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$$

Step 2: The formation of a precipitate of iron(II) hydroxide:

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$$

Steps 1 and 2 of the wet corrosion process are summarised in Figure 5.1.17.

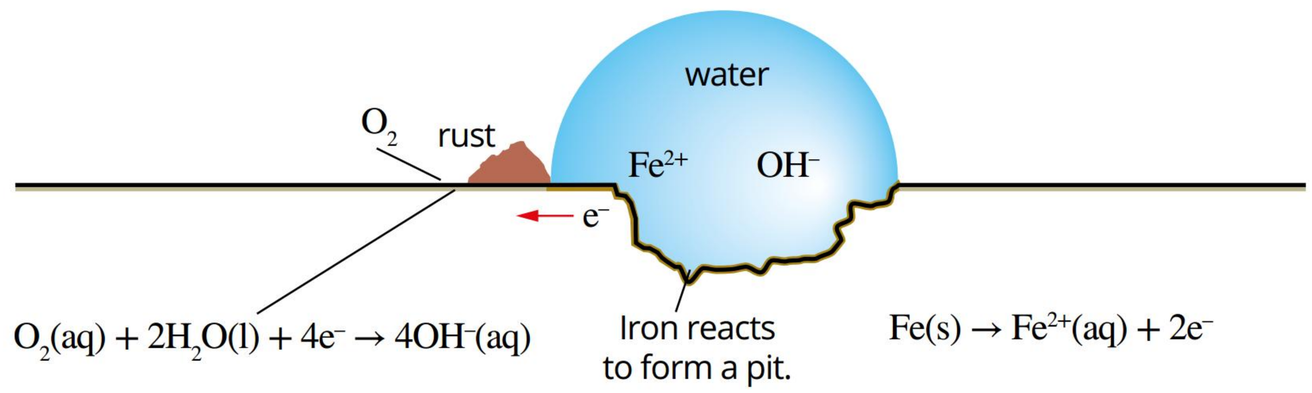


FIGURE 5.1.17 During wet corrosion, electrons are transferred through the iron from the area where oxidation occurs to the area where reduction occurs. Ions flow through the water droplets.

Step 3: Further oxidation of iron(II) hydroxide occurs in the presence of oxygen and water to produce iron(III) hydroxide, a red-brown precipitate:

$$4Fe(OH)_2(s) + O_2(aq) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$$

Step 4: In air, the iron(III) hydroxide loses water to form hydrated iron(III) oxide ($Fe_2O_3 \cdot xH_2O$), which is known as rust.

The porous rust easily flakes off the surface of the iron, exposing the iron underneath to further oxidation.

The wet corrosion of iron is accelerated if the water contains dissolved ions. This is particularly evident in coastal areas where iron objects are exposed to seawater. The presence of dissolved ions in the water increases its conductivity, which results in an increase in the rate of iron corrosion.

5.1 Review

SUMMARY

- Redox reactions are electron transfer reactions; one or more reactant substances lose electrons that are accepted by other reactants.
- The loss of electrons by a reactant is known as oxidation; the gain of electrons by a reactant is known as reduction.
- The loss and gain of electrons by reactants occur simultaneously, so oxidation and reduction processes cannot occur independently of one another.
- Reduction and oxidation processes can each be represented via half-equations; the sum of the reduction and oxidation half-equations is used to generate the full redox equation.
- Oxidising agents cause the oxidation of other substances—they are themselves reduced in redox reactions; reducing agents cause the reduction of other substances—they are themselves oxidised in redox reactions.
- The relative reactivity of metals is represented in the metal reactivity series.
  - The metal reactivity series can be represented as a simple list of metals or as a list of reversible redox half-equations between metals and their ions.
  - The half-equations involving stronger reducing agents (the ones more easily oxidised) appear higher in the list than those involving weaker reducing agents.
  - The reactivity series can be used to predict whether a metal displacement process is likely to occur.
- Metal displacement reactions involve the transfer of electrons from a more reactive metal to the cations of a less reactive metal in solution.
- Some metals readily corrode via oxidation processes. These processes can be characterised as 'dry corrosion' or 'wet corrosion'.
  - Dry corrosion refers to the oxidation of a metal by oxygen gas.
  - Wet corrosion involves both oxygen gas and water.

KEY QUESTIONS

Describe

1 Define the following terms.

a oxidation

b reduction

c redox reaction

2 Describe:

a an oxidising agent

b a reducing agent.

3 Use Figure 5.1.9 on page 153 to list the following in order of increasing reducing strength: Mg, Ag, Ni, Sn, Li and Cu.

4 Identify each of the following half-equations as involving either oxidation or reduction.

a $Na(s) \rightarrow Na^{+}(aq) + e^{-}$

b $Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$

c $S(s) + 2e^{-} \rightarrow S^{2-}(aq)$

d $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

Apply

5 Summarise redox reactions by using the following terms to complete the sentences: gains, loses, I_2, I^{-}, reduced, oxidised.

When a reducing agent, such as Fe, reacts with an oxidising agent, such as _____, an ionic compound is formed. The reducing agent _____ electrons (is _____) and at the same time, the oxidising agent _____ electrons (is _____). In this case, the products are Fe^{2+} and _____, which form FeI_2.

6 Explain how water is involved in the wet corrosion of iron, using equations to support your answer.

7 Distinguish between a reducing agent and an oxidising agent, using the reversible half-equation $Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$ to illustrate your answer.

Continued over page

5.1 Review *continued*

Analyse

8 When a strip of magnesium metal is placed in a blue solution containing copper(II) ions ($Cu^{2+}(aq)$), crystals of copper appear and the solution soon becomes paler in colour.

- **a** Show that this reaction is a redox reaction by identifying the substance that is oxidised and the one that is reduced.
- **b** Construct a half-equation for the oxidation reaction.
- **c** Construct a half-equation for the reduction reaction.
- **d** Construct an overall redox equation.
- **e** Identify the oxidising agent and the reducing agent in the overall redox equation.
- **f** Explain why the solution loses some of its blue colour as a result of the reaction.

9 Balance the following half-equations and then classify each as an oxidation or a reduction reaction.

- **a** $Fe(s) \rightarrow Fe^{2+}(aq)$
- **b** $Ag^{+}(aq) \rightarrow Ag(s)$
- **c** $K(s) \rightarrow K^{+}(aq)$
- **d** $O_2(g) \rightarrow O^{2-}(aq)$

10 Refer to the list of reversible redox reactions in Figure 5.1.9 on page 153 to predict whether the following reactions will spontaneously occur.

- **a** Silver metal is placed in a nickel(II) nitrate solution.
- **b** A strip of aluminium is placed in a sodium chloride solution.
- **c** Magnesium is added to a solution of iron(II) sulfate.
- **d** Zinc is placed in a tin(II) sulfate solution.
- **e** A piece of tin is placed in a silver nitrate solution.
- **f** Lead(II) nitrate solution is poured into a beaker containing zinc granules.

11 Use the list of reversible redox reactions in Figure 5.1.9 on page 153 to predict whether a reaction will occur in each of the following situations. Construct an overall ionic equation for each reaction that you predict will occur.

- **a** Copper(II) sulfate solution is stored in an aluminium container.
- **b** Sodium chloride solution is stored in a copper container.
- **c** Silver nitrate solution is stored in a zinc container.

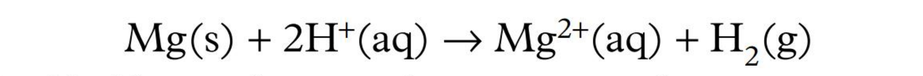
12 A student wished to store some tin(II) nitrate solution in a metal container. The student had the choice of a copper container, a nickel container or a zinc container. State which of these three containers would be the most suitable for storage of the tin(II) nitrate solution, and explain why the other two containers could not be used. Support your answer with chemical equations.

5.2 Identifying redox reactions

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

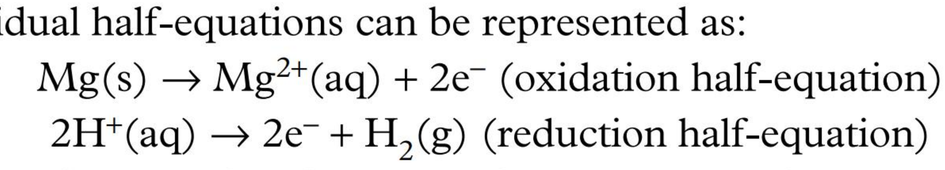
- assign oxidation numbers to atoms in elements, compounds and polyatomic ions
- use oxidation numbers to determine whether a reaction is a redox reaction
- understand oxidation and reduction in terms of changes in oxidation numbers of atoms
- use oxidation numbers to identify oxidising and reducing agents
- recognise combustion reactions as redox reactions by using oxidation numbers to identify oxidising and reducing agents
- use oxidation numbers to name ionic compounds involving transition metal ions
- use oxidation numbers to identify conjugate redox pairs.

How can you tell if a particular chemical reaction is in fact a redox reaction? In the reaction of magnesium, Mg(s), with hydrochloric acid, HCl(aq), you can see that the charges on the Mg(s) and H^+(aq) ions change during the reaction. The net ionic equation for this reaction is:



$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

The individual half-equations can be represented as:

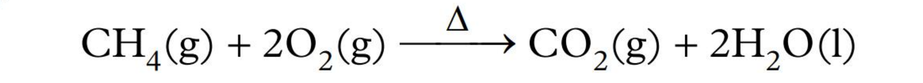


$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \text{ (oxidation half-equation)}$$

$$2H^+(aq) \rightarrow 2e^- + H_2(g) \text{ (reduction half-equation)}$$

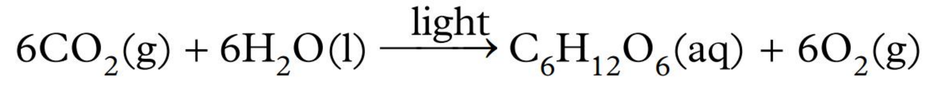
Clearly, there is a transfer of electrons from the magnesium metal to the H^+ ions, which changes the charge on both species. This change in charge is indicative of a redox reaction.

But what about a combustion reaction? For example, the combustion of methane (CH_4):



$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(l)$$

Or consider photosynthesis, which can be represented by this overall chemical equation:



$$6CO_2(g) + 6H_2O(l) \xrightarrow{\text{light}} C_6H_{12}O_6(aq) + 6O_2(g)$$

Are these redox reactions? The substances represented in each of these equations are all molecular substances and have no net charge. You cannot say by simple inspection that there has been a change in charge of any of the atoms involved and you cannot readily determine if electron transfer has occurred. Therefore, you cannot easily determine if these reactions are redox reactions.

OXIDATION NUMBERS

It turns out that the combustion and photosynthesis reactions shown above are redox reactions and that a transfer of electrons has occurred between atoms of the reactant molecules. So the question remains; how can you tell if a chemical reaction is a redox reaction? And how can you tell which atom or molecule has been oxidised (and is therefore the reducing agent), and which atom or molecule has been reduced (and is therefore the oxidising agent)?

You do this by assigning **oxidation numbers** to atomic species or to individual atoms within molecular species. The oxidation number of an atom in a substance represents the charge that an atom would have if it was an ion.

The key to identifying whether a chemical reaction is a redox reaction is to determine if the oxidation number of any atoms changes during the reaction.

If the oxidation number of a particular atom changes during a chemical reaction, you can say that the atom has undergone oxidation or reduction and that the reaction is a redox reaction.

Rules for assigning oxidation numbers

Oxidation numbers are also referred to as **oxidation states**. The rules for assigning oxidation numbers (or states) to atoms in substances are outlined in Table 5.2.1. In the examples shown in the table, the oxidation number of an element is placed above its symbol. The plus or minus sign precedes the number and so distinguishes the oxidation number from the charge on an ion where the sign is generally placed after the number. For example, the oxide ion (O^{2-}) has a charge of 2– and an oxidation number of –2. While the values are the same in this instance, it is important to remember that oxidation states do not always indicate a charge on the species.

TABLE 5.2.1 Rules for determining oxidation numbers of elements in compounds

Rule	Examples
1 The oxidation number of a free element is zero.	$\overset{0}{Na}, \overset{0}{C}, \overset{0}{Cl_2}, \overset{0}{P_4}$
2 The oxidation number of a simple ion is equal to the charge on the ion.	$\overset{+1}{Na^+}, \overset{-1}{Cl^-}, \overset{+2}{Mg^{2+}}, \overset{-2}{O^{2-}}, \overset{+3}{Al^{3+}}, \overset{-3}{N^{3-}}$
3 In compounds, some elements have oxidation numbers that are regarded as fixed, except in a few exceptional circumstances.	
a Main group metals have an oxidation number equal to the charge on their ions.	ionic compounds: $\overset{+1}{K}Cl, \overset{+2}{Mg}SO_4$
b Hydrogen has an oxidation number of +1 when it forms compounds with non-metals. Exception: In metal hydrides, the oxidation number of hydrogen is –1.	compounds of H: $\overset{+1}{H_2}O$ metal hydrides: $Na\overset{-1}{H}, Ca\overset{-1}{H_2}$
c Oxygen usually has an oxidation number of –2. Exceptions: In compounds with fluorine, oxygen has a positive oxidation number. In peroxides, oxygen has an oxidation number of –1. **d** Halogens: The oxidation number of fluorine is –1 in all of its compounds. The oxidation number of the other halogens in their compounds (i.e. Cl, Br, I) is also –1, except when they are involved in compounds with O or another halogen above them in group 17 of the periodic table.	compounds of O: $H_2\overset{-2}{O}$ compounds of O and F: $\overset{+2}{O}F_2$ peroxides: $H_2\overset{-1}{O_2}, Ba\overset{-1}{O_2}$ fluorine compounds: $\overset{+1}{H}\overset{-1}{F}, \overset{+2}{O}\overset{-1}{F_2}$ other halogen compounds: $\overset{+1}{H}\overset{-1}{Cl}, \overset{+1}{Cl_2}\overset{-2}{O}, \overset{+5}{Cl}\overset{-1}{F_5}$
4 The sum of the oxidation numbers of all atoms in a neutral compound is zero.	$\overset{+4}{C}\overset{-2}{O_2}$ Note that in CO_2, the oxidation number of each O atom is –2; since the sum of the oxidation numbers of all atoms must equal zero for a neutral compound, you can easily calculate that the oxidation number of the single C atom must be +4.
5 The sum of the oxidation numbers of all atoms in a polyatomic ion is equal to the charge on the ion.	$\overset{+6}{S}\overset{-2}{O_4}^{2-}, \overset{-3}{N}\overset{+1}{H_4}^{+}$
6 The most electronegative element is assigned the negative oxidation number.	$\overset{+2}{O}\overset{-1}{F_2}, \overset{+6}{S}\overset{-1}{F_6}$

Oxidation numbers have no physical meaning and they do not indicate a formal charge nor are they representative of the physical or chemical properties of the substance. However, they are a useful tool for identifying which atoms have been oxidised and which atoms have been reduced. It is important to remember that the oxidation number is always calculated for just one atom of the element.

> If the oxidation number of an atom has increased after a chemical reaction, that atom has undergone oxidation.
>
> If the oxidation number of an atom has decreased after a chemical reaction, that atom has undergone reduction.

Calculating oxidation numbers of atoms in compounds

The common oxidation numbers of the first 32 elements in their compounds are shown in the periodic table in Figure 5.2.1. Transition metals and some non-metals can have a range of oxidation states. These are usually calculated after applying the rules for all other elements in the compound.

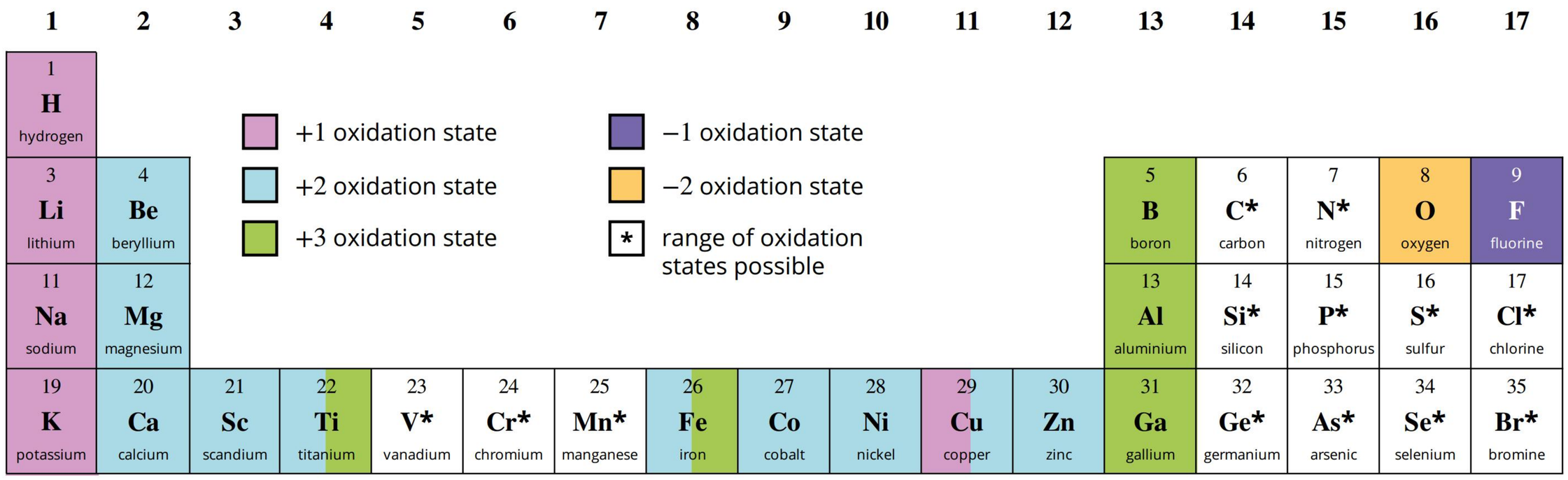


FIGURE 5.2.1 A part of the periodic table showing the most common oxidation states of some elements.

For a compound containing several elements, you can use algebra and the rules given in Table 5.2.1 to calculate the oxidation number of an element.

Worked example 5.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 5.2.1 on page 162 to determine the oxidation number of each element in potassium perchlorate ($KClO_4$).

Thinking	Working
Identify an element that has a set value.	K is a main group metal in group 1. Applying rule 3a, the oxidation number of K is +1.
Identify any other elements that have set values.	According to rule 3c, in compounds, oxygen has an oxidation number of –2 unless attached to fluorine or in a peroxide.
Use algebra to work out the oxidation number of other elements.	Let the oxidation number of Cl in $KClO_4$ be x. Solve the sum of the oxidation numbers for x: $+1 + x + 4 \times (-2) = 0$ $+1 + x - 8 = 0$ $x - 7 = 0$ $x = +7$
Show oxidation numbers above the elements in the formula.	$\overset{+1}{K}\overset{+7}{Cl}\overset{-2}{O_4}$ Note that the oxidation number of oxygen is written as –2 (not as –8), even though there are four oxygen atoms in the formula. Confirming rule 4 from Table 5.2.1, you can see that the sum of oxidation numbers of all atoms in the compound is zero (i.e. $+1 + 7 + (4 \times -2) = 0$).

➤ Try yourself 5.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 5.2.1 on page 162 to determine the oxidation number of each element in sodium nitrate ($NaNO_3$).

USING OXIDATION NUMBERS

The oxidation number concept is a valuable tool that can be used to:

- identify whether a chemical reaction is a redox reaction (remember, if there is no change of oxidation number for all atoms involved in the reaction, excluding spectator ions, then the reaction is not a redox reaction)
- determine which substance is the oxidising agent and which is the reducing agent
- name ionic compounds involving cations derived from transition metals
- identify conjugate redox pairs.

Using oxidation numbers to identify oxidising and reducing agents

You have already noted that a change in oxidation number of an atom after a chemical reaction indicates that the reaction is a redox reaction. You also know that:

- an increase in oxidation number of an atom means that the atom has been oxidised
- a decrease in oxidation number of an atom means that the atom has been reduced.

Finally, you also know that an oxidising agent is itself reduced, and that a reducing agent is itself oxidised. You can therefore use this knowledge to assist in determining which reactant is the oxidising agent and which reactant is the reducing agent.

At the beginning of this chapter, you were alerted to a number of everyday processes that are redox reactions. Combustion reactions, where fuel is burnt in order to produce heat while giving off CO_2 and water, are examples of redox reactions that are very important in our society. The equation for the burning of carbon in excess oxygen is:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

At first glance, the reaction may not seem like a redox reaction because none of the species are ionic compounds, so it is not clear which reactant is losing or gaining electrons. By using oxidation numbers, you can identify both the oxidation and reduction processes in the reaction:

$$\overset{0}{C}(s) + \overset{0}{O_2}(g) \rightarrow \overset{+4}{C}\overset{-2}{O_2}(g)$$

The carbon is oxidised because its oxidation number increases from 0 to +4, and the oxygen is reduced because its oxidation number decreases from 0 to –2. Furthermore, since the carbon is oxidised, it is identified as the reducing agent—it has enabled, or caused, the reduction of oxygen. Similarly, since oxygen has been reduced, it is identified as the oxidising agent—it has enabled, or caused, the oxidation of carbon.

In this way, the use of oxidation numbers allows you to look at a chemical reaction and determine whether it is a redox reaction and then, more specifically, to determine which reactant is the oxidising agent and which is the reducing agent.

ℹ Remember that the oxidation number of an element is calculated for just one atom of that element.

Worked example 5.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDISING AND REDUCING AGENTS

Determine whether the following is a redox reaction and (if so) identify the oxidising and reducing agents:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Thinking	Working
Determine the oxidation numbers for each element in the equation.	$\overset{-4}{C}\overset{+1}{H_4}(g) + 2\overset{0}{O_2}(g) \rightarrow \overset{+4}{C}\overset{-2}{O_2}(g) + 2\overset{+1}{H_2}\overset{-2}{O}(l)$
Assess if the oxidation number of any element has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of C has increased from –4 to +4, so the carbon in CH_4 has been oxidised. The oxidation number of O has decreased from 0 to –2, so oxygen has been reduced. The oxidation number of H has remained unchanged, so hydrogen has not undergone oxidation or reduction.
The compound or element containing the atom that has been oxidised is designated as the reducing agent. The compound or element containing the atom that has been reduced is designated as the oxidising agent.	CH_4 is identified as the reducing agent (it caused the reduction of O_2) and O_2 is identified as the oxidising agent (it caused the oxidation of CH_4).

➤ Try yourself 5.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDISING AND REDUCING AGENTS

Determine whether the following is a redox reaction and (if so) identify the oxidising and reducing agents:

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$$

Using oxidation numbers to name ionic compounds

As you learnt in Units 1 and 2, **transition elements** can form ions with a number of different charges. This means that many transition metals have variable oxidation numbers (or oxidation states). For example, there are two compounds that can be called iron chloride: $FeCl_2$ and $FeCl_3$.

Using the rules in Table 5.2.1 on page 162, you can see that the chloride ion has an oxidation number of –1. In $FeCl_2$, this means the oxidation number of iron is +2, whereas in $FeCl_3$, the oxidation number is +3.

To distinguish between the two iron chlorides, you insert Roman numerals to represent the appropriate oxidation number in the name:

- $FeCl_2$ is more correctly named iron(II) chloride.
- $FeCl_3$ is more correctly named iron(III) chloride.

For elements that can have variable oxidation states, the use of a Roman numeral in the name indicates the specific oxidation state of the element.

Using oxidation numbers to identify conjugate redox pairs

When a half-equation is written for an oxidation reaction, the reactant, a reducing agent, loses electrons. The product is an oxidising agent. You refer to the reactant and the product that it forms as a **conjugate redox pair**.

For example, consider the half-equation for the oxidation of zinc:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

Zinc metal (Zn) is a reducing agent and forms $Zn^{2+}(aq)$, which is an oxidising agent. Zn(s) and $Zn^{2+}(aq)$ form a conjugate redox pair $Zn(s)/Zn^{2+}(aq)$.

In the $Zn(s)/Zn^{2+}(aq)$ conjugate redox pair, the oxidation number of zinc increases from 0 to +2. The increase in the oxidation number of zinc indicates that it is an oxidation half-reaction.

For the reduction half-equation, the reactant is an oxidising agent and will gain electrons. The product formed is a reducing agent. Therefore, another conjugate redox pair is present in the redox reaction.

For example, consider the half-equation for the reduction of $Ag^+(aq)$:

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

$Ag^+(aq)$ is an oxidising agent and forms Ag(s), which is a reducing agent. $Ag^+(aq)$ and Ag(s) are a conjugate redox pair. In this case, the oxidation number of silver decreases from +1 to 0, indicating that this is a reduction half-equation. It is worth noting at this point that the list of redox equations you used in Figure 5.1.9 on page 153 is a list of redox conjugate pairs of metals and their ions.

The relationship between changes in oxidation numbers and conjugate redox pairs can be seen by following the colour-coding in the equation shown in Figure 5.2.2. One conjugate redox pair is red and the other one is blue.

When listing conjugate redox pairs, the states of both the oxidising and reducing agents should be included.

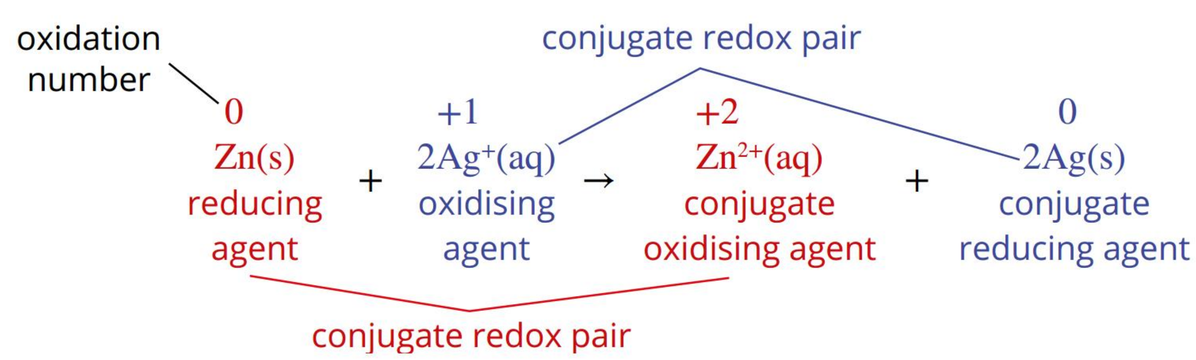
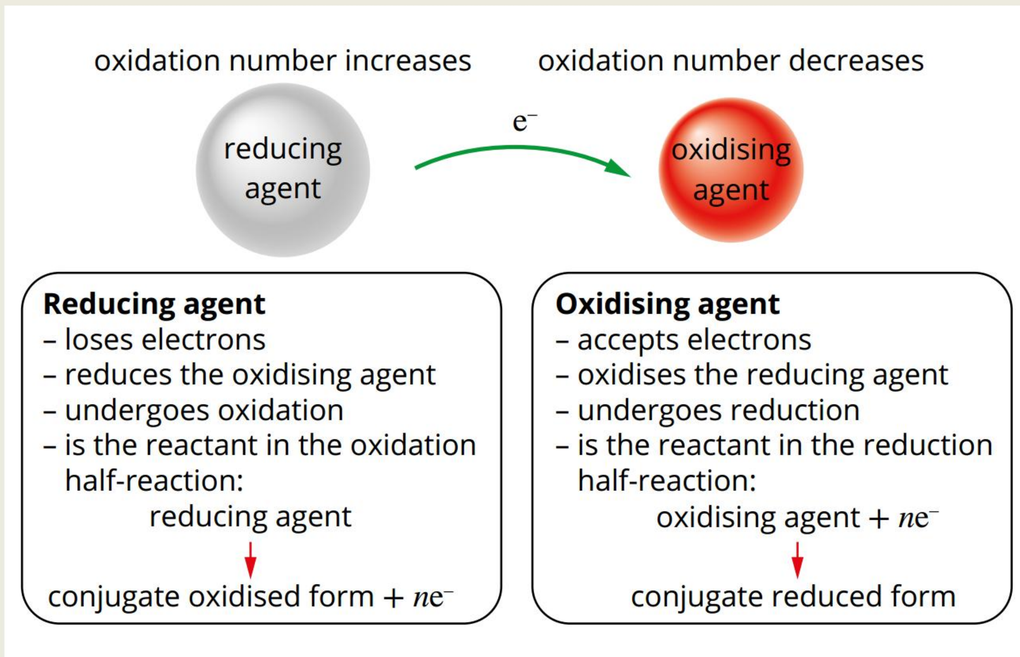


FIGURE 5.2.2 The change in oxidation numbers seen in conjugate redox pairs. For each redox reaction, there are two conjugate redox pairs.

5.2 Review

SUMMARY

- Oxidation numbers are calculated according to a set of rules, including:
  - free elements have an oxidation number of 0
  - in ionic compounds composed of simple monatomic ions, the oxidation number is equal to the charge on the ion
  - hydrogen in a compound usually has an oxidation number of +1
  - oxygen in a compound usually has an oxidation number of –2
  - the sum of the oxidation numbers in a neutral compound is 0
  - the sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.
- An increase in the oxidation number of an element in a reaction indicates oxidation has occurred.
- A decrease in the oxidation number of an element in a reaction indicates reduction has occurred.
- For oxidation to occur, there must be a corresponding reduction.
- In a combustion reaction, the fuel is oxidised by oxygen, making the fuel the reducing agent and oxygen the oxidising agent.
- If there is no change in the oxidation number of any atoms involved in the equation for a particular reaction, then that reaction is not a redox reaction.
- The oxidation number (or oxidation state) is used to name ionic compounds containing transition metal ions. (Note: the Roman numeral representation of the oxidation number is used.)
- A conjugate redox pair consists of an oxidising agent (a reactant) and the reducing agent (a product) that is formed when the oxidising agent gains electrons.
- In a redox reaction, if a conjugate redox pair consists of a reducing agent (a reactant) and the oxidising agent (a product) that is formed when the reducing agent loses electrons, then the oxidation number of the reducing agent (the reactant) increases.
- A summary of redox reaction terms is shown in the following diagram.



KEY QUESTIONS

Describe

1 Define the oxidation number of an atom in a substance.

2 State how the oxidation number of the following are determined:

a an element

b a monatomic ion.

3 Deduce the correct missing term by completing the following statements using either 'decreases' or 'increases'.

a If the oxidation number of an atom _____ after a chemical reaction, that atom has undergone oxidation.

b If the oxidation number of an atom _____ after a chemical reaction, that atom has undergone reduction.

4 Determine the oxidation state of the metal ion in the following ionic compounds.

a $CuCl_2$

b $Mg(OH)_2$

c Cr_2O_3

d $AgNO_3$

Continued over page

5.2 Review *continued*

5 Determine which one or more of the following substances contain manganese in the +6 oxidation state: $MnCl_2$, $MnCl_3$, MnO_2, $KMnO_4$, K_2MnO_4.

Apply

6 Calculate the oxidation numbers of the underlined element in the following compounds or ions.

a $\underline{Ca}O$
b $H\underline{S}O_4^-$
c $\underline{Mn}O_4^-$
d $\underline{N}H_4^+$
e $\underline{S}O_3^{2-}$
f $Na\underline{N}O_3$
g $\underline{N_2}O$
h $K_2\underline{Cr_2}O_7$

7 Indicate the correct conjugate redox pairs for each redox reaction by completing the following table.

Redox reaction	Conjugate redox pair (oxidation process)	Conjugate redox pair (reduction process)
$Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$		
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$		
$2K(s) + Cl_2(g) \rightarrow 2K^+(s) + 2Cl^-(s)$		

8 Write the correct name for each of the following transition metal compounds, using Roman numerals to indicate the oxidation number of the transition metal.

a $Cu(NO_3)_2$
b Fe_2O_3
c V_2O_5
d $Cr_2(SO_4)_3$

Analyse

9 Determine which carbon compound is the least oxidised by calculating the oxidation number of carbon in the following compounds.

CO, CO_2, CH_4, CO_3^{2-}

10 In question **5**, you determined the oxidation state of manganese in the following compounds: $MnCl_2$, $MnCl_3$, MnO_2, $KMnO_4$, K_2MnO_4. Use your knowledge of their oxidation numbers to match these compounds to their names in the table below.

Name	Formula
manganese(IV) oxide	
potassium manganate(VI)	
manganese(II) chloride	
manganese(III) bromide	
potassium manganate(VII)	

11 Compare oxidation numbers of atoms on both sides of the following equations to identify the oxidising and reducing agents.

a $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
b $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
c $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$
d $2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$
e $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

12 Use oxidation numbers to determine whether the underlined element in each of the following reactions has been oxidised, reduced or neither oxidised or reduced.

a $2FeCl_3(aq) + SnCl_2(aq) \rightarrow 2FeCl_2(aq) + \underline{Sn}Cl_4(aq)$
b $\underline{Zn}CO_3(s) \rightarrow ZnO(s) + CO_2(g)$
c $3\underline{Br_2}(aq) + 2Al(s) \rightarrow 2AlBr_3(s)$

13 Each of the following half-equations has a mistake in it, so it does not correctly match the description given. For each half-equation, determine what the error is and then state the correct half-equation that matches the description given.

a oxidation of silver: $Ag(s) + e^- \rightarrow Ag^+(aq)$
b oxidation of copper: $Cu(s) + e^- \rightarrow Cu^{2+}(aq) + 3e^-$
c oxidation of zinc metal: $Zn(aq) \rightarrow Zn^{2+}(s) + 2e^-$
d reduction of iodine: $I_2(aq) + e^- \rightarrow I^-(aq)$
e reduction of $Na^+(aq)$: $Na(s) - e^- \rightarrow Na^+(aq)$

5.3 Balancing complex redox reactions using half-equations

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- balance half-equations for complex redox reactions in acidic conditions
- balance overall redox equations for complex reactions in acidic conditions.

Not all oxidation and reduction half-equations involve simple ions and their elements. Many interesting redox reactions, such as the 'elephant's toothpaste' reaction shown in Figure 5.3.1, can be quite complicated. For example, they often contain numerous reactants and products, have large stoichiometric coefficients, and typically involve polyatomic ions and other reactants and products that have oxygen and hydrogen in their formulas. The overall balanced equation for this example is $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$. Determining the individual half-equations for reactions like this can be quite complex. In this reaction, a solid potassium iodide catalyst is added to a hydrogen peroxide solution. Red colouring has been added for effect.

FIGURE 5.3.1 The 'elephant's toothpaste' demonstration involves a redox reaction in which hydrogen peroxide is both the reducing agent and the oxidising agent.

In this module, you will learn how to balance complex redox equations in a few short steps.

BALANCING REDOX EQUATIONS FOR COMPLEX REACTIONS

The methods used for balancing chemical equations may break down when dealing with complex redox equations. Consider the following unbalanced chemical equations:

$$Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$$
$$As_4O_6(s) + MnO_4^{-}(aq) \rightarrow AsO_4^{3-}(aq) + Mn^{2+}(aq)$$

Attempting to balance these equations using the approaches outlined in Units 1 and 2 would not be suitable. For a start, it is not immediately obvious if either of these reactions is a redox reaction; and if they are, it is not clear which substances are undergoing oxidation and which substances are undergoing reduction.

The first of these equations is particularly interesting because the element oxygen does not even appear on the right-hand side of the equation despite being present on the left-hand side. Finally, both of these equations contain complex, polyatomic, oxy-anions, which usually require special attention when balancing equations.

For these reasons, there is a different approach to balancing complex chemical equations using a combination of assigning oxidation numbers and using half-equations. While you have some experience in balancing simple half-equations, you need to be able to tackle more complex half-equations before attempting to balance full redox equations.

You will first learn how to balance more complex half-equations and then you will learn how to balance full redox equations. In both cases, only reactions in acidic conditions are considered.

Steps for balancing complex half-equations (acidic conditions)

Half-equations that involve atoms or simple ions can be written quite easily. For example, knowing that magnesium metal is oxidised to form Mg^{2+} ions in solution, you can write the half-equation as:

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$$

However, half-equations involving polyatomic ions are usually less obvious. The anaesthetic nitrous oxide or laughing gas (N_2O) can be prepared by the reduction of nitrate ions in an acidic solution:

$$2NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow N_2O(g) + 5H_2O(l)$$

Such half-equations can be constructed by following the steps below. The reduction of nitrate ions will be used to illustrate this process.

1 Balance all atoms except oxygen and hydrogen in the half-equation. Since the compound of N on the right-hand side is N_2O, you need two NO_3^- ions on the left-hand side:

$$2NO_3^- \rightarrow N_2O$$

2 Balance the oxygen atoms by adding H_2O molecules to one side of the half-equation. Since there are now six O atoms on the left-hand side, you need to add five H_2O molecules on the right-hand side to balance the O atoms:

$$2NO_3^- \rightarrow N_2O + 5H_2O$$

3 Balance the hydrogen atoms by adding H^+ ions to one side of the half-equation. Since there are now 10 H atoms on the right-hand side, you need to add 10 H^+ ions on the left-hand side:

$$2NO_3^- + 10H^+ \rightarrow N_2O + 5H_2O$$

4 Balance the charge on both sides of the half-equation by adding electrons (e^-) to the side with the greater positive charge. In this case, the total charge on the left-hand side is $(2 \times -1) + (10 \times +1) = +8$, while the total charge on the right-hand side is zero. Make the charges equal by adding eight electrons to the left-hand side:

$$2NO_3^- + 10H^+ + 8e^- \rightarrow N_2O + 5H_2O$$

The total charge on both sides is now equal and the total number (and type) of atoms is also equal. This half-equation is now balanced.

5 Indicate whether each substance exists as a dissolved solute or as a solid, liquid or gas by inserting the appropriate state symbols:

$$2NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow N_2O(g) + 5H_2O(l)$$

It is important to note that half-equations and full redox equations must be fully balanced, as shown in Figure 5.3.2. The number of atoms of each element must be equal on each side, just like balancing any other chemical equation. In addition, the total charge on each side of the equation must also be equal. You should also note that the charges being equal does not mean they must be zero.

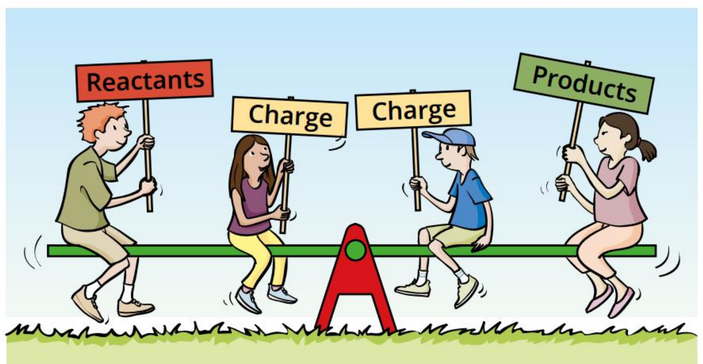


FIGURE 5.3.2 In balanced half-equations and overall redox equations, the number of atoms of each element is equal on both sides and the total charge on each side is equal.

Steps for balancing full redox equations (acidic conditions)

The steps you use to balance chemical equations for complex redox reactions are outlined below. The five steps you used above for balancing half-equations have been included in Step 3 below.

Balancing complex redox equations is best demonstrated via examples; the unbalanced equations introduced at the beginning of this module are used as examples below.

1 Calculate oxidation numbers of each atom to determine which (if any) atoms are undergoing oxidation and which atoms are undergoing reduction. (If no atoms change their oxidation number, then the reaction is not a redox reaction and the use of the half-equation approach is not valid.)

2 Split the chemical equation into two unbalanced half-equations, one containing the reactants and products for the oxidation process and one containing the reactants and products for the reduction process.

3 Construct and balance each half-equation. They must be both mass-balanced and charge-balanced.

- **i** Balance all atoms except oxygen and hydrogen.
- **ii** Balance O atoms by adding H_2O molecules to one side of the half-equation.
- **iii** Balance H atoms by adding H^+ ions to one side of the half-equation.

iv Balance the charge on both sides of the half-equation by adding electrons (e^-) to the side with the greater positive charge.

v Add state symbols for all reactants and products.

4 Add the two half-equations together to obtain the final balanced redox equation.

i Electrons cannot appear in the final redox equation. If there are unequal numbers of electrons in the half-equations, multiply each half-equation by whole numbers to ensure that the electrons lost in the oxidation half-equation equal the electrons gained in the reduction half-equation.

ii Simplify the redox equation by cancelling any species that occurs on both sides.

iii Check that you have the same number of each type of atom on each side, and check that the total charge on the left-hand side is the same as the total charge on the right-hand side.

To balance the following equation, you need to follow the steps outlined above.

$$Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$$

Step 1: Calculating the oxidation numbers for each atom using the rules in Table 5.2.1 gives the following for the left-hand side (LHS) and the right-hand side (RHS) of the equation:

LHS: Cr = +6 (rule 5); O = −2 (rule 3c); Fe = +2 (rule 2)

RHS: Cr = +3 (rule 2); Fe = +3 (rule 2)

The Fe atom has increased its oxidation number and has therefore undergone oxidation; Cr has decreased its oxidation number and has therefore undergone reduction.

Step 2: Split the reaction into unbalanced oxidation and reduction half-equations:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) \text{ (unbalanced oxidation half-equation)}$$

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq) \text{ (unbalanced reduction half-equation)}$$

Step 3: Complete and balance each half-equation. Balance elements other than O and H first, then add H_2O molecules and H^+ ions to balance the O and H atoms. Finally, add electrons (e^-) to balance charge.

For the oxidation half-equation, the Fe atoms are already balanced and no O or H atoms are present, so you only need to add one electron to the RHS:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

You take the same approach with the reduction half-equation. There are two Cr atoms on the LHS, so you need to place a 2 in front of Cr^{3+} on the RHS:

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

You will note that there are seven O atoms on the LHS, so you must place seven H_2O molecules on the RHS:

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

This results in 14 H atoms on the RHS, so you place 14 H^+ ions on the LHS:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

The total charge on the LHS is 12+. The total charge on the RHS is 6+. You therefore place six electrons on the LHS:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Step 4: You now add the two half-equations together to obtain the full redox equation. First, however, you will note that there are uneven numbers of electrons appearing in both half-equations. You therefore need to multiply each half-equation by appropriate factors to ensure that there is an equal number of electrons lost in the oxidation half-equation as there is gained in the reduction half-equation. You do this by multiplying the oxidation half-equation by 6; this gives six electrons on the RHS of this half-equation to match the six electrons on the LHS of the reduction half-equation. When you add these two half-equations together, the electrons will cancel:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$$

This equation is now both mass-balanced and charge-balanced.

The steps for balancing complex redox half-equations must be carried out in sequence for the process to work.

Worked example 5.3.1

BALANCING COMPLEX REDOX EQUATIONS (ACIDIC CONDITIONS)

Balance the following equation using half-equations.

$$As_4O_6(s) + MnO_4^-(aq) \rightarrow AsO_4^{3-}(aq) + Mn^{2+}(aq)$$

Thinking	Working
Step 1. Calculate the oxidation numbers for each atom in the chemical equation (using the rules in Table 5.2.1 on page 162). Determine which atoms are undergoing oxidation and which are undergoing reduction.	$\overset{+3}{A}S_4\overset{-2}{O}_6(s) + \overset{+7}{M}n\overset{-2}{O}_4^-(aq) \rightarrow \overset{+5}{A}S\overset{-2}{O}_4^{3-}(aq) + \overset{+2}{M}n^{2+}(aq)$ The oxidation number of As has increased from +3 to +5, so the arsenic in As_4O_6 has been oxidised. The oxidation number of Mn in MnO_4^- has decreased from +7 to +2, so manganese has been reduced. The oxidation number of O has remained unchanged, so oxygen has not undergone oxidation or reduction.
Step 2. Split the reaction into two unbalanced half-equations, one containing the reactants and products for the oxidation process and one containing the reactants and products for the reduction process.	$As_4O_6(s) \rightarrow AsO_4^{3-}(aq)$ (unbalanced oxidation half-equation) $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$ (unbalanced reduction half-equation)
Step 3. Formulate and balance each half-equation. They must be both mass-balanced and charge-balanced. Balance elements other than O and H first, then add H_2O molecules and H^+ ions to balance the O and H atoms. Finally, add electrons (e^-) to balance charge.	For the oxidation half-equation, four As atoms appear on the LHS, so you place a '4' in front of AsO_4^{3-} on the RHS: $As_4O_6(s) \rightarrow 4AsO_4^{3-}(aq)$ This gives 16 O atoms on the RHS. You therefore add 10 H_2O molecules to the LHS to balance O atoms (there are already six O atoms on the LHS): $As_4O_6(s) + 10H_2O(l) \rightarrow 4AsO_4^{3-}(aq)$ This gives 20 H atoms on the LHS. You therefore add 20 H^+ ions to the RHS: $As_4O_6(s) + 10H_2O(l) \rightarrow 4AsO_4^{3-}(aq) + 20H^+(aq)$ The total charge on the LHS is zero. The total charge on the RHS = 4 × –3 + 20 × +1 = +8. You therefore need to add $8e^-$ to the RHS: $As_4O_6(s) + 10H_2O(l) \rightarrow 4AsO_4^{3-}(aq) + 20H^+(aq) + 8e^-$ Taking the same approach with the reduction half-equation, you will note the Mn atoms are already balanced. You need to place four H_2O molecules on the RHS to balance the O atoms. This gives eight H atoms on the RHS; you therefore place eight H^+ ions on the LHS. You balance the charge by adding five electrons to the LHS: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
Step 4. Add the two half-equations together to obtain the final balanced redox equation.	You will note that there are uneven numbers of electrons appearing in both half-equations. You therefore need to multiply each half-equation by appropriate factors to ensure that there is an equal number of electrons lost in the oxidation half-equation as there is gained in the reduction half-equation. You do this by multiplying the oxidation half-equation by 5 and the reduction half-equation by 8, thus giving a total of 40 electrons in each half-equation. When you add these two half-equations together, the electrons will cancel: $5As_4O_6(s) + 50H_2O(l) + 8MnO_4^-(aq) + 64H^+(aq) \rightarrow$ $20AsO_4^{3-}(aq) + 100H^+(aq) + 8Mn^{2+}(aq) + 32H_2O(l)$ This equation is now both mass-balanced and charge-balanced and simplifies to the following (after cancelling H_2O molecules and H^+ ions on both sides): $5As_4O_6(s) + 18H_2O(l) + 8MnO_4^-(aq) \rightarrow 20AsO_4^{3-}(aq) + 36H^+(aq) + 8Mn^{2+}(aq)$

➤ Try yourself 5.3.1

BALANCING COMPLEX REDOX EQUATIONS (ACIDIC CONDITIONS)

Construct the balanced redox equation for the reaction between ethanol and the dichromate ion to produce ethanoic acid and the chromium(III) ion, as represented by the following unbalanced equation:

$$C_2H_6O(l) + Cr_2O_7^{2-}(aq) \rightarrow C_2H_4O_2(aq) + Cr^{3+}(aq)$$

5.3 Review

SUMMARY

- The following steps must be taken to balance redox half-equations under acidic conditions.
  1. Balance all atoms except oxygen and hydrogen.
  2. Balance the oxygen atoms by adding H_2O molecules to one side of the half-equation.
  3. Balance the hydrogen atoms by adding H^+ ions to one side of the half-equation.
  4. Balance the charge on both sides of the half-equation by adding electrons (e^-) to the side with the greater positive charge.
  5. Add state symbols for all reactants and products.
- To construct an overall equation, add the oxidation half-equation and the reduction half-equation, making sure that the number of electrons used in reduction equals the number of electrons released during oxidation.
- When combining oxidation and reduction half-equations under acidic conditions, any $H^+(aq)$ and $H_2O(l)$ that appear on both sides of the arrow should be cancelled down.

KEY QUESTIONS

Describe

1 Select the word in bold that completes the following sentences correctly.

a Electrons appear on the **left-hand/right-hand** side of a half-equation for oxidation half-equations.

b Electrons appear on the **left-hand/right-hand** side of a half-equation for reduction half-equations.

2 List the steps for balancing redox half-equations in acidic conditions.

Apply

3 Determine half-equations for the:

a reduction of MnO_2 to Mn^{2+}

b reduction of MnO_4^- to MnO_2

c reduction of SO_4^{2-} to H_2S

d oxidation of SO_2 to SO_4^{2-}

e oxidation of H_2S to S

f oxidation of SO_3^{2-} to SO_4^{2-}.

4 When zinc powder is sprinkled into an acidified solution of potassium dichromate ($K_2Cr_2O_7$), a reaction occurs that produces zinc ions and chromium(III) ions in solution. The potassium ions are spectator ions and the net reaction is between Zn(s) and $Cr_2O_7^{2-}(aq)$ ions.

a Determine the oxidation half-equation for the reaction.

b Determine the reduction half-equation for the reaction.

c Use your answers to parts **a** and **b** to construct a balanced equation for the overall reaction.

5 Construct the half-equations and the balanced overall equation for the reaction in which:

a a solution containing iron(II) ions is oxidised by an acidified solution containing hydrogen peroxide (H_2O_2). The products include iron(III) and water.

b a solution containing sulfite ions (SO_3^{2-}) reacts with an acidified solution of permanganate ions (MnO_4^-) to produce a colourless solution containing sulfate ions and manganese(II) ions.

c manganese dioxide (MnO_2) reacts with concentrated hydrochloric acid to form chlorine gas and a solution containing manganese(II) ions.

Analyse

6 Classify each of the following as 'redox' or 'not redox', and state the reasons for your classification.

a $Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$

b $LiCl(aq) + AgNO_3(aq) \rightarrow LiNO_3(aq) + AgCl(s)$

c $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

d $C(s) + O_2(g) \rightarrow CO_2(g)$

e $C_{12}H_{22}O_{11}(s) + 2H_2SO_4(aq) \rightarrow 11C(s) + CO_2(g) + 2SO_2(g) + 13H_2O(l)$

Continued over page

5.3 Review *continued*

7 As a result of a traffic accident, residents in a Gold Coast suburb had to be evacuated when toxic fumes leaked from a container of sodium dithionite ($Na_2S_2O_4$). The dithionite ion reacts with water according to the equation:

$2S_2O_4^{2-}(aq) + H_2O(l) \rightarrow S_2O_3^{2-}(aq) + 2HSO_3^-(aq)$

a State the oxidation number of the sulfur in the following ions.

i $S_2O_4^{2-}$

ii $S_2O_3^{2-}$

iii HSO_3^-

b Determine half-equations for the oxidation and reduction reactions that occur when sodium dithionite is mixed with water.

8 Balance each of the following equations by determining the two half-equations that are occurring and balancing the electrons.

a $SO_3^{2-}(aq) + Ce^{4+}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + Ce^{3+}(aq) + H^+(aq)$

b $Cr_2O_7^{2-}(aq) + H^+(aq) + I^-(aq) \rightarrow Cr^{3+}(aq) + I_2(aq) + H_2O(l)$

c $ClO_4^-(aq) + SO_2(aq) + H_2O(l) \rightarrow Cl^-(aq) + SO_4^{2-}(aq) + H^+(aq)$

GO TO ➤ **Practical Investigation 2**

Chapter review

05

KEY TERMS

conjugate redox pair
direct corrosion
displace
dry corrosion
half-equation
main group metal
metal displacement reaction
oxidant
oxidation
oxidation number
oxidation state
oxidised
oxidising agent
reactivity series of metals
redox reaction
reduced
reducing agent
reductant
reduction
spontaneous redox reaction
transition element
wet corrosion

KEY QUESTIONS

Describe

1 List the overall steps for balancing full redox equations in acidic conditions.

2 State why oxidation and reduction must occur simultaneously in redox reactions.

3 State what process the metal atoms have undergone when pure metals are extracted from their oxide ores.

4 Determine whether each of the following statements is true or false.

a Groups 1 and 2 metal ions, such as Na^+, are reducing agents because they tend to lose electrons.

b Group 17 molecules, such as I_2, can be oxidising agents.

c Non-metal ions, such as Cl^-, can be reducing agents because they can lose electrons.

d Metals, such as Cu, can be oxidising agents because they can gain electrons.

5 Deduce the correct missing terms by completing the following sentences that describe oxidation and reduction.

Oxidation and reduction occur together. Oxidation occurs when an atom or ion _____ electrons to form a _____ ion, such as when a calcium atom, with a condensed electron configuration of [Ar]$4s^2$,_____ electrons to form a Ca^{2+} ion. Reduction occurs when an atom _____ electrons to form a _____ ion or when a cation _____ electrons to become a neutral atom. An example is when a bromine atom, with _____ electrons in its valence shell, _____ an electron to form a _____ ion.

6 List the following in terms of increasing reducing strength.

K, Cu, Sn, Mg, Zn

Apply

7 Consider the following half-equations and the overall equation for the reaction between sodium metal and a solution of silver ions.

$$Na(s) \rightarrow Na^+(aq) + e^-$$
$$Ag^+(aq) + e^- \rightarrow Ag(s)$$
$$Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$$

Determine which one of the following sets of statements correctly describes this redox reaction.

A Na(s) is the reducing agent, $Ag^+(aq)$ is the oxidising agent, sodium metal is oxidised.

B Na(s) is the oxidising agent, $Ag^+(aq)$ is the reducing agent, sodium metal is reduced.

C Na(s) is the reducing agent, $Ag^+(aq)$ is the oxidising agent, sodium metal is reduced.

D $Na^+(aq)$ is the oxidising agent, Ag(s) is the reducing agent, sodium metal is oxidised.

8 Magnesium reacts with nickel(II) ions according to the following equation:

$$Mg(s) + Ni^{2+}(aq) \rightarrow Mg^{2+}(aq) + Ni(s)$$

Determine which one of the following is the correct set of conjugate redox pairs for this reaction.

A $Mg^{2+}(aq)/Mg(s)$ and $Ni^{2+}(aq)/Ni(s)$

B $Ni(s)/Mg^{2+}(aq)$ and $Ni^{2+}(aq)/Mg(s)$

C $Mg(s)/Ni(s)$ and $Ni^{2+}(aq)/Mg^{2+}(aq)$

D $Mg(s)/Ni^{2+}(aq)$ and $Ni(s)/Mg^{2+}(aq)$

9 Determine which one of the following alternatives describes what happens when sodium and oxygen react.

A Each sodium atom gains one electron.

B Each sodium atom loses one electron.

C Each oxygen atom gains one electron.

D Each oxygen atom loses one electron.

10 Determine which one of the following redox equations has not been balanced correctly.

A $Zn^{2+}(aq) + Mg(s) \rightarrow Zn(s) + Mg^{2+}(aq)$
B $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$
C $Fe^{2+}(aq) + Zn(s) \rightarrow Fe(s) + Zn^{2+}(aq)$
D $Ag^{+}(aq) + Cu(s) \rightarrow Ag(s) + Cu^{2+}(aq)$

11 Deep-sea divers sometimes report that the metal on vessels they find on the seabed does not appear to have corroded. Determine which one of the following might contribute to the lack of corrosion.

A Deep-sea creatures eat iron oxide.
B A lack of light prevents corrosion from occurring.
C There is little oxygen dissolved in the water near the seabed.
D The concentration of dissolved salt in the sea decreases with increasing depth.

12 Determine which of the following reactions is not a redox reaction.

A $H_2SO_4(aq) + CaCO_3(s) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$
B $H_2SO_4(aq) + Mg(s) \rightarrow MgSO_4(aq) + H_2(g)$
C $H_2SO_4(aq) + Fe(s) + 2H^{+}(aq) \rightarrow SO_2(g) + Fe^{2+}(aq) + 2H_2O(l)$
D $C_{12}H_{22}O_{11}(s) + 2H_2SO_4(aq) \rightarrow 11C(s) + CO_2(g) + 2SO_2(g) + 13H_2O(l)$

13 Calculate the oxidation number of sulfur in each of the following compounds.

a SO_2
b H_2S
c SO_3
d Na_2SO_3
e $Na_2S_2O_3$

14 Demonstrate your understanding of oxidation numbers and elements by completing the following table.

Compound	Element	Oxidation number
H_2O_2		–1
HCO_3^-		+4
HNO_3	N	
$KMnO_4$		+7
Cr_2O_3	Cr	
N_2O_4	N	

15 Copper bowls and trays can be decorated by etching patterns on them using concentrated nitric acid. The overall reaction is:

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

a Determine what the oxidation number of copper is:
  i before the reaction
  ii after the reaction.
b Determine the oxidation number of nitrogen:
  i before the reaction
  ii after the reaction.
c Name the oxidising agent and the reducing agent in this process.

16 State the name of each of the following transition metal compounds, using the oxidation number of the transition metal in your answer.

a Cu_2O
b VCl_3
c $Co(NO_3)_2$
d MnO_2

17 Complete the summary below as you balance the half-equation for the reduction of NO_3^- to NO_2 in an acidic solution:

$$NO_3^-(aq) \rightarrow NO_2(g)$$

Step	Task	How it's done	Half-equation
1	Balance nitrogens.		$NO_3^-(aq) \rightarrow NO_2(g)$
2	Balance oxygens by adding _____.	Add _____ H_2O molecule(s) to right-hand side of the equation.	
3	Balance hydrogens by adding _____.	Add _____ H^+ ion(s) to _____ of the equation.	
4	Balance charge by adding _____.	Charge on left-hand side = _____ Charge on right-hand side = _____ Add _____ e^- to _____ of the equation.	
5	Add state symbols to give the final half-equation.	Give the appropriate states for each reactant and product in the equation.	

18 During each of the following analyses, redox reactions occurred. Construct half-equations for the oxidation and reduction reactions. Use these half-equations to construct an overall equation for each reaction.

- **a** Zinc was reduced by reacting it with a solution of Pb^{2+} ions. Lead metal was precipitated and Zn^{2+} ions were formed.
- **b** The amount of Fe^{2+} ions in iron tablets was determined by oxidising them to Fe^{3+} ions using an acidified solution of MnO_4^- ions. The MnO_4^- ions were reduced to Mn^{2+} ions during the reaction.
- **c** Sulfur dioxide (SO_2), a preservative in dried fruit, was determined in aqueous solution by oxidation to SO_4^{2-} using an aqueous solution of I_2. Iodide (I^-) ions were produced.
- **d** An acidified solution of bleach, which contains OCl^- ions, was titrated against a solution of I^- ions. The reaction products included Cl^- and I_2.

19 In dry cells commonly used in torches, an electric current is produced from the reaction of zinc metal with solid manganese oxide (MnO_2). During this reaction, Zn^{2+} ions and solid Mn_2O_3 are formed.

- **a** Calculate the oxidation numbers for the zinc and manganese species in this reaction.
- **b** Identify the oxidising agent and the reducing agent in this reaction.
- **c** Write the half-equations for the oxidation and reduction reactions.
- **d** Write the overall equation for the reaction.

20 The following equations are not balanced.

- **i** Identify the species that has been reduced and the species that has been oxidised.
- **ii** Show balanced half-equations for the oxidation and reduction reactions.
- **iii** Combine the half-equations to show a balanced overall equation.

- **a** $Ce^{4+}(aq) + H_2S(g) \rightarrow Ce^{3+}(aq) + S(s) + H^+(aq)$
- **b** $NO_3^-(aq) + H^+(aq) + Cu(s) \rightarrow NO(g) + H_2O(l) + Cu^{2+}(aq)$
- **c** $H_2O_2(aq) + Br^-(aq) + H^+(aq) \rightarrow Br_2(l) + H_2O(l)$
- **d** $MnO_2(s) + H^+(aq) + S(s) \rightarrow Mn^{2+}(aq) + H_2O(l) + SO_2(g)$

21 Consider the following equation for a redox reaction.

$Cl_2(aq) + Zn(s) \rightarrow ZnCl_2(aq)$

- **a** State the oxidation numbers of the substances in this equation.
- **b** Identify the substance that is oxidised.
- **c** Write the half-equation for the reduction reaction.

Analyse

22 Sort the following substances in order of increasing oxidation states of nitrogen.

NO, K_3N, N_2O_4, N_2O, $Ca(NO_3)_2$, N_2O_3, N_2

23 Consider the following products that are made during the wet corrosion of iron. Classify them in terms of the oxidation state of iron in the compound.

$Fe(OH)_3(s)$, $Fe_2O_3.xH_2O(s)$, $Fe(OH)_2(s)$, $Fe^{2+}(aq)$,

24 Iron reacts with hydrochloric acid according to the ionic equation:

$$Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$$

- **a** Identify the species that has been oxidised in this reaction.
- **b** Identify the product of oxidation.
- **c** Construct the half-equation for the oxidation reaction.
- **d** Identify the oxidising agent.
- **e** Construct the half-equation for the reduction reaction.

25 Calcium metal that is exposed to the air forms an oxide coating.

- **a** Determine the formula of calcium oxide.
- **b** Deduce which reactant has been oxidised in this reaction.
- **c** Write a balanced half-equation for the oxidation reaction.
- **d** Determine which reactant has been reduced in this reaction.
- **e** Write a balanced half-equation for the reduction reaction.
- **f** Write an overall equation for this redox reaction.

26 In the following redox reactions, determine which species have been oxidised and which have been reduced.

- **a** $Cu^{2+}(aq) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(aq)$
- **b** $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
- **c** $PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$
- **d** $Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$
- **e** $Pb^{2+}(aq) + Fe(s) \rightarrow Pb(s) + Fe^{2+}(aq)$

27 During the combustion of ethane (C_2H_6) in oxygen gas, carbon dioxide and water are produced.

- **a** Calculate the oxidation numbers of the reactants and products in this reaction.
- **b** Identify the species that has been oxidised and the species that has been reduced and support your answers with a reason.
- **c** Identify the oxidising agent and the reducing agent in this reaction.

28 An unknown metal is placed in solutions of aluminium nitrate and iron(II) sulfate. After a period of time, the metal is found to have reacted with the iron(II) sulfate solution, but not the aluminium nitrate solution. Determine a possible identity of the unknown metal.

29 Iron nails are placed into solutions of $CuSO_4$, $MgCl_2$, $Pb(NO_3)_2$ and $ZnCl_2$. Predict in which solutions you would expect a coating of another metal to appear on the nail. Explain your answer.

30 Determine whether elements from the following groups would be more likely to be oxidised or reduced when they take part in chemical reactions with the other group.

Group A: sodium, calcium and magnesium

Group B: sulfur, oxygen and chlorine

31 Solid ammonium dichromate decomposes to form chromium(III) oxide, nitrogen gas and steam.

a Calculate the oxidation numbers of chromium and nitrogen in the reactant ammonium dichromate ($(NH_4)_2Cr_2O_7$) and the products Cr_2O_3 and N_2. Identify which reactants have been reduced and which have been oxidised.

b Complete and balance the following half-equations.

i $NH_4^+(s) \rightarrow N_2(g)$

ii $Cr_2O_7^{2-}(s) \rightarrow Cr_2O_3(s)$

c Identify each of the half-equations in part **b** as either reduction or oxidation processes and explain your answer in terms of oxidation numbers.

d Construct the balanced overall equation for the reaction that occurs.

e Identify the conjugate redox pairs for the reaction.

Interpret

32 Create a concept map that shows the links between the following terms: redox reactions, oxidising agent, reducing agent, electrons, oxidation, reduction.

33 Vitamin C ($C_6H_8O_6$) is an essential vitamin to maintain good health. The amount of vitamin C present in food can be determined by titration against a solution of iodine (I_2), using starch as an indicator. The products for this redox reaction are $C_6H_6O_6$ and iodide ions (I^-). Write the two half-equations and the overall equation for the reaction occurring in acidic conditions.

Data analysis

DATA SET 1

The information below applies to Questions 1–4. Please refer to data provided on page 11 of the Formula and Data Book in answering the following questions.

Students conducted a series of reactions between metal sulfate solutions, Ag_2SO_4, $CuSO_4$ and $ZnSO_4$, and some clean pieces of metal. Observations of a reaction or no reaction in the nine test tubes were recorded. The results are shown in the table below.

The students noted that there was no reaction, as expected, between each metal and its sulfate salt (Test 2, Test 6 and Test 7).

Results of mixing three metals and their metal sulfate solutions:

	Ag_2SO_4	$CuSO_4$	$ZnSO_4$
Cu	Test 1	Test 2	Test 3
	Reaction	No reaction	No reaction
Zn	Test 4	Test 5	Test 6
	Reaction	Reaction	No reaction
Ag	Test 7	Test 8	Test 9
	No reaction	No reaction	No reaction

Question 1 (1 mark)

Explain why silver metal showed no reaction with $CuSO_4$ and $ZnSO_4$.

Question 2 (1 mark)

Identify the oxidising agent in Test 5.

Question 3 (3 marks)

Write the half-equations and hence a balanced redox equation for the reaction in Test 4.

Question 4 (3 marks)

List the order of reactivity of the three metals, from lowest to highest. Refer to the data to justify your answer.

CHAPTER 06

Galvanic cells

By the end of this chapter, you will know how galvanic cells generate electricity from chemical reactions. You will become familiar with the components of galvanic cells (e.g. the anode, the cathode and the salt bridge) and know how to predict the direction of electron flow in the external circuit of a galvanic cell.

You will be introduced to half-cells and know how to determine the standard electrode (reduction) potential, E^o, of a half-cell. You will then use E^o data to calculate the potential difference, or cell potential (E^o_{cell}), of galvanic cells.

Finally, you will see how experimental data from galvanic cells can be used to make predictions about the spontaneity of a reaction and compare the relative strengths of oxidising and reducing agents.

Syllabus subject matter

Topic 2 • Oxidation and reduction

ELECTROCHEMICAL CELLS

- Explain that electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit that allows electrons to move from the anode (oxidation reaction) to the cathode (reduction reaction). **6.1**
- Discriminate between a galvanic and an electrolytic cell. **6.1**

GALVANIC CELLS

- Identify that galvanic cells generate an electrical potential difference from a spontaneous redox reaction. **6.2**
- Explain that galvanic cells can be represented as cell diagrams, including anode and cathode half-equations. **6.1, 6.2**
- Explain that oxidation occurs at the negative electrode (anode) and reduction occurs at the positive electrode (cathode). **6.1**
- Explain that two half-cells can be connected by a salt bridge to create a galvanic cell, e.g. Mg, Zn, Fe and Cu and solutions of their ions. **6.1, 6.2**
- Identify the essential components of a galvanic cell, including the oxidation and reduction half-cells, the positive and negative electrodes and their solutions of their ions, the flow of electrons and the movement of ions, and the salt bridge. **6.1, 6.2**
- Sketch a galvanic cell and label the essential components. **6.1, 6.2**

STANDARD ELECTRODE POTENTIAL

- Describe the standard hydrogen electrode. **6.2**
- Explain the term *standard electrode (reduction) potential*, E^o. **6.2**
- Identify the limitations associated with standard electrode (reduction) potentials, E^o. **6.3**
- Calculate cell potential, E^0_{cell} (Formula: $E^0_{cell} = E^0_{reduction\ half\text{-}cell} - E^0_{oxidation\ half\text{-}cell}$). **6.2, 6.3**

- Apply standard electrode potentials to determine the relative strength of oxidising and reducing agents. **6.2**
- Analyse data, including standard electrode potentials, to make predictions about the spontaneity of a reaction and to compare electrochemical cells. **6.2, 6.3**

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6.1 Portable power

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that a galvanic cell uses a spontaneous redox reaction to convert chemical energy into electrical energy
- identify the key components of a galvanic cell and explain how the cell operates
- construct half-equations for the processes that occur within the compartments of a galvanic cell and use the half-equations to construct an overall equation for the cell reaction
- identify differences between galvanic and electrolytic cells.

Electronic devices such as mobile phones, notebook computers, cameras and hearing aids all depend on small portable sources of electricity: cells and batteries (Figure 6.1.1). Portable energy in the form of cells and batteries enables you to operate electrical equipment without the restrictions of a power cord.

The demand for electronic devices has stimulated the production of a variety of cells, from tiny button cells for watches and calculators to the huge batteries used to operate lighthouses. The energy provided by cells and batteries may be more expensive than energy from other sources, such as fossil fuels, but this cost is offset by their convenience. The biggest innovations in batteries in recent years has been for electric vehicles and storage of solar energy in homes and industry. There has been much research and development to make batteries that are more efficient, that last longer and leave a smaller environmental footprint.

In this module, you will learn how cells are constructed, and how they provide you with a source of electrical energy. You will also learn to differentiate between galvanic and electrolytic cells.

FIGURE 6.1.1 Your way of life depends on cells and batteries.

ELECTROCHEMICAL CELLS

An **electrochemical cell** is a device in which chemical energy is transformed into electrical energy, or vice versa. A **galvanic cell** is a type of electrochemical cell in which chemical energy is transformed into electrical energy. The cells in your mobile phone and laptop are galvanic cells. By contrast, an **electrolytic cell** is a type of electrochemical cell in which electrical energy is used to induce chemical change. This type of cell is used for electroplating. For example, tin plating on iron to protect it from corrosion. Rechargeable batteries also rely on the principles of electrolytic cells.

Table 6.1.1 shows the key difference between galvanic and electrolytic cells. Electrolytic cells will be discussed in detail in Chapter 7, and we consider galvanic cells in more detail here.

TABLE 6.1.1 A comparison of two types of electrochemical cells

	Galvanic cell	Electrolytic cell
Energy considerations	converts chemical energy (from chemical reactions) into electrical energy	converts electrical energy into chemical energy by inducing chemical reactions
Reaction type	spontaneous redox reaction	non-spontaneous redox reaction
Energy source	no external power source is required; an electrical current is produced	requires an external power source; an electrical current induces chemical change
Examples/ applications	batteries, fuel cells, corrosion prevention	electroplating, metal extraction, electrolysis of water to produce hydrogen and oxygen, recharging batteries

INTRODUCING GALVANIC CELLS

In everyday language, we refer to galvanic cells as batteries. In Chemistry, a **battery** is a device that stores and supplies energy through chemical reactions, converting chemical energy into electrical energy. It generally comprises one or more galvanic cells, arranged in series or parallel, to achieve the desired voltage and current output. A combination of cells connected in series is used to obtain a higher potential difference or 'voltage'.

Figure 6.1.2 shows how you can produce a galvanic cell from simple laboratory equipment.

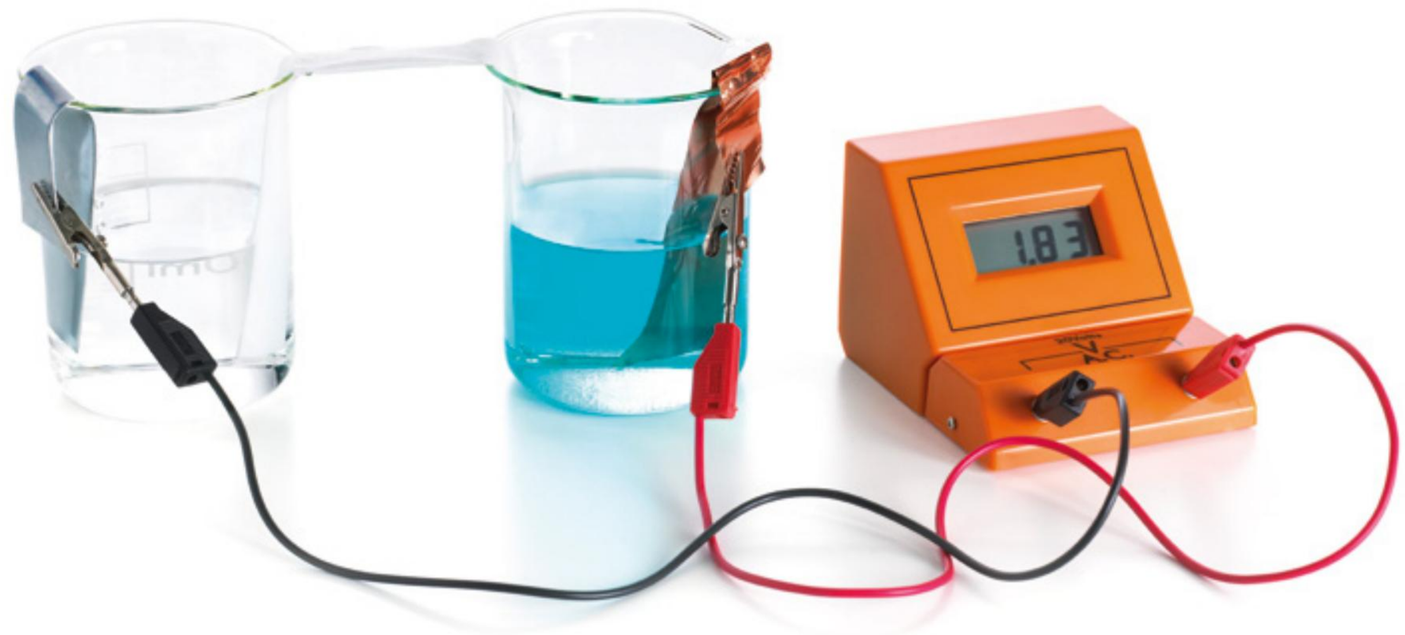


FIGURE 6.1.2 Construction of a galvanic cell from simple laboratory equipment

In Figure 6.1.3, you can see a diagram of a cell called the Daniell cell, named after the scientist who invented it in 1836, John Daniell. The cell produces an electric current that flows through the wire and light globe. This part of the cell is called the **external circuit**. The globe converts the electrical energy of the current into light and heat.

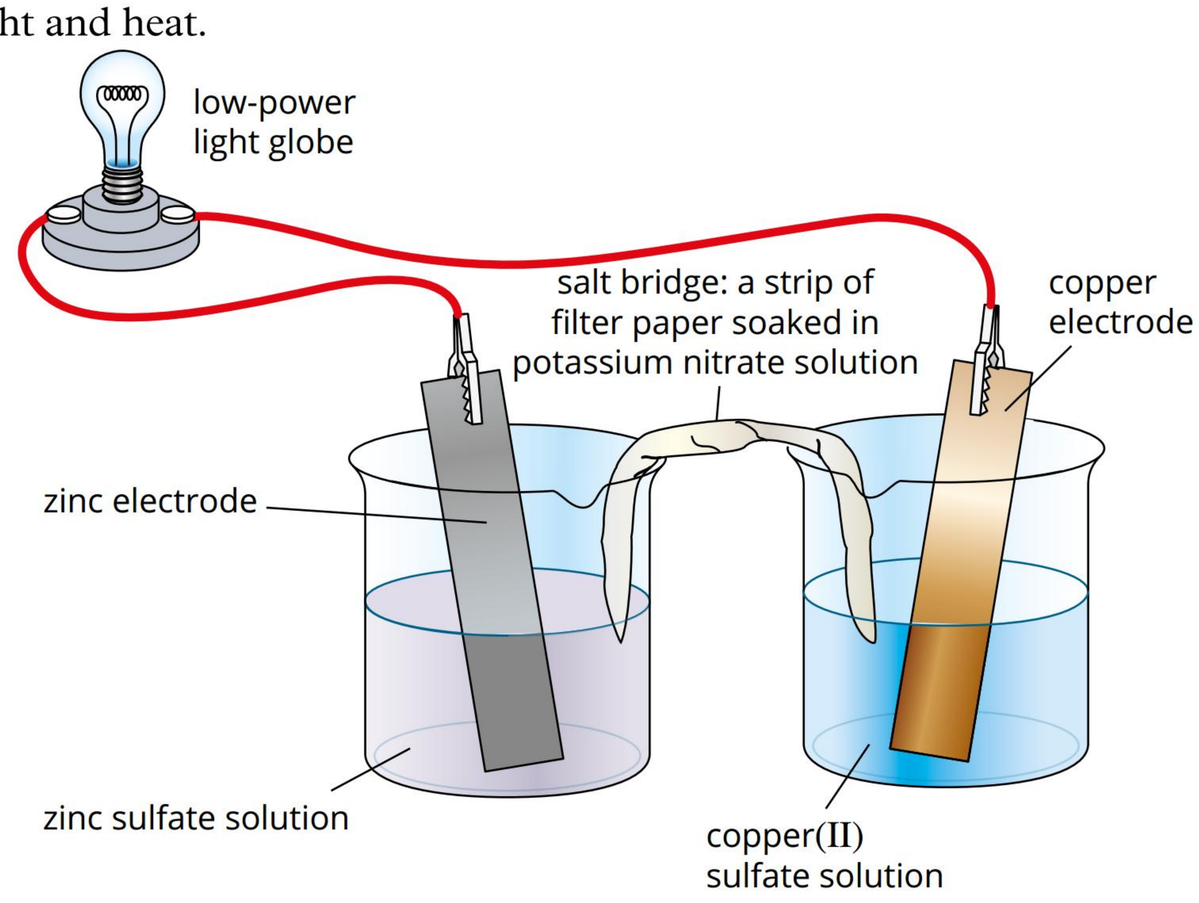


FIGURE 6.1.3 The Daniell cell is a type of galvanic cell.

The current flows because a chemical reaction is taking place in the cell. If you leave the cell with a light globe connected for several hours, you will see evidence of this reaction occurring: the zinc metal corrodes, the copper metal becomes covered with a furry dark brown deposit and the blue copper(II) sulfate solution loses some of its colour.

If you replace the light globe with a **galvanometer** (an instrument for detecting electric current), the galvanometer will indicate that electrons flow from the zinc **electrode** through the wire to the copper electrode. Current flows only if the two halves of the cell are connected by a **salt bridge**. A salt bridge is often made from filter paper soaked in a relatively unreactive **electrolyte**, such as a solution of potassium nitrate.

These observations lead to the following explanations about what is occurring in a galvanic cell.

- The reaction in the cell is a redox reaction because electrons are being transferred.
- The zinc electrode corrodes because the zinc metal forms zinc ions in solution:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

- The oxidation of the zinc metal releases electrons, which flow through the external wire to the copper electrode.
- Electrons are accepted by copper(II) ions in the solution when the ions collide with the copper electrode. A reduction reaction occurs:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

- The copper metal that is formed deposits on the electrode as a dark brown coating.

In this cell, there is a transformation of chemical energy to electrical energy. Figure 6.1.4 shows the processes that occur during the operation of the cell. The equation for the overall reaction is found by adding the two half-equations:

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

Note that when these half-equations are added together, there are the same number of electrons (two) on each side of the equation so the electrons are cancelled out and do not appear in the final equation. From Chapter 5, you will recognise this overall reaction as a redox reaction, with one substance being oxidised and one substance being reduced.

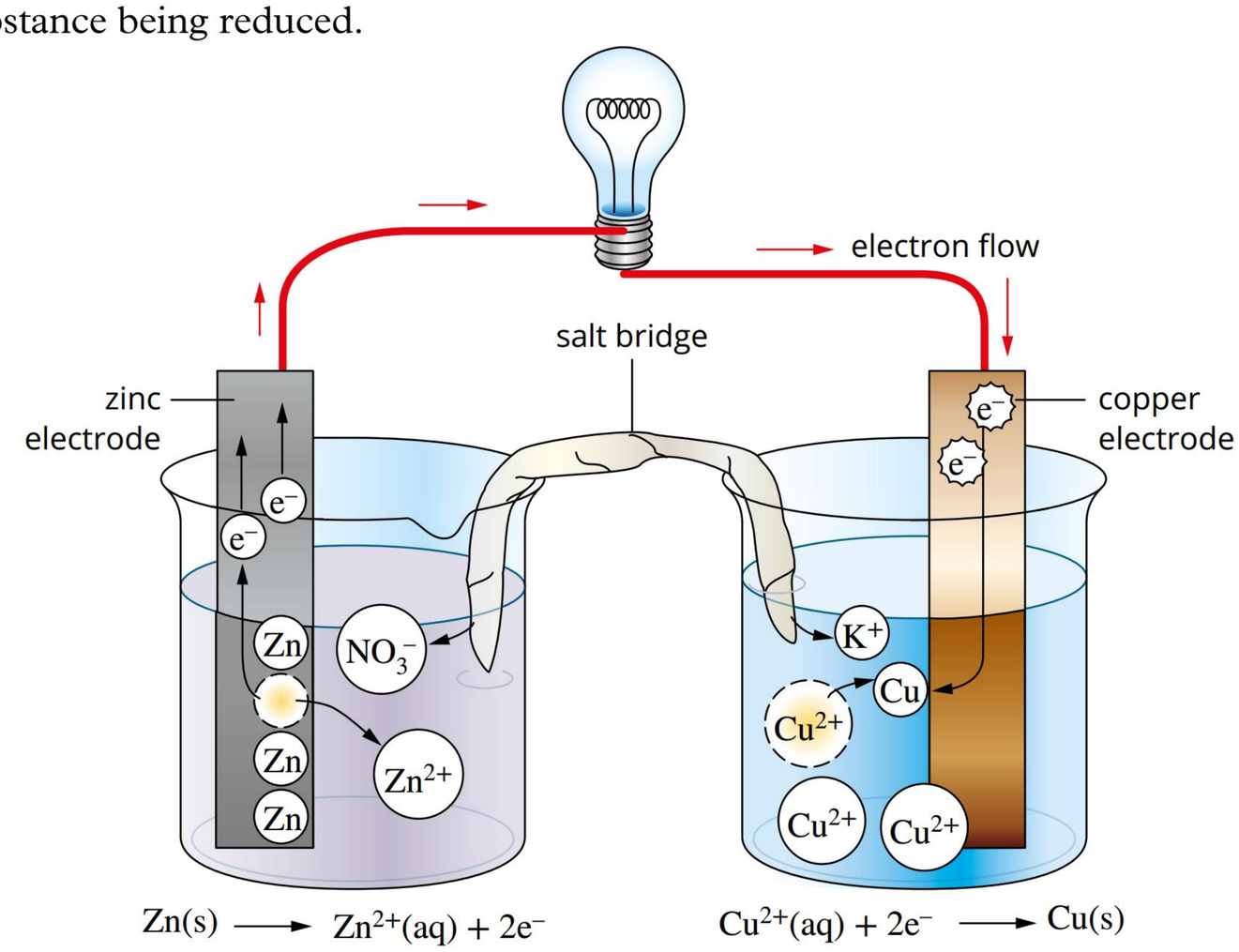


FIGURE 6.1.4 A representation of the electrode reactions in a Daniell cell. The salt bridge contains potassium nitrate solution.

This redox reaction is described as a **spontaneous reaction** because it occurs naturally, without the need for an external energy source.

Copper(II) ions act as the oxidising agent, or oxidant, and zinc metal acts as the reducing agent, or reductant.

A chemical that causes another substance to be oxidised is called an oxidising agent and is itself reduced in a redox reaction.

Conversely, a chemical that causes another substance to be reduced is called a reducing agent and is itself oxidised in a redox reaction.

FIGURE 6.1.5 $Cu^{2+}(aq)$ ions in blue-coloured copper(II) sulfate solution reacting directly with a strip of zinc metal

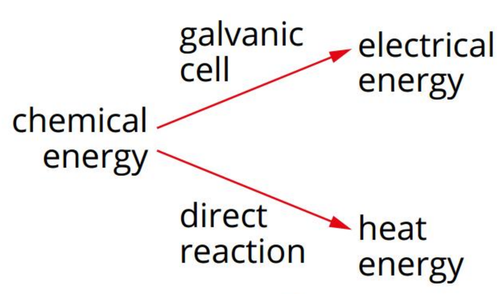


FIGURE 6.1.6 Energy transformations that occur when reactants are separated in a galvanic cell and when the reactants react directly

ENERGY TRANSFORMATIONS IN DIRECT AND GALVANIC PROCESSES

In Chapter 5, metal displacement reactions were discussed, with the more reactive metal being oxidised and the less reactive metal cation being reduced. You may have seen a metal displacement reaction similar to the one that occurs in a Daniell cell if you have copper-plated a piece of metal, such as zinc. When zinc is immersed in an aqueous solution containing $Cu^{2+}(aq)$ ions, the metal becomes coated in dark brown copper. This can be seen in Figure 6.1.5. At the same time, thermal energy is produced, which escapes into the surrounding environment as heat.

The overall equation for this metal displacement reaction is:

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

This reaction is an example of a spontaneous exothermic reaction. If the reactants are allowed to come into direct contact with each other, their chemical energy is transformed directly into thermal energy. However, in a galvanic cell, the half-reactions occur in separate compartments, and the electrons are transferred by the external circuit so that chemical energy is transformed into electrical energy.

The energy changes that occur in galvanic cells and when reactants undergo direct reaction are summarised in Figure 6.1.6.

HOW A GALVANIC CELL OPERATES

A galvanic cell is designed so that half-reactions occur in two separate compartments of the cell. Because the oxidising agent and reducing agent do not come into direct contact with each other, electrons can only be transferred through an external circuit connecting the negative and positive electrodes.

This flow of electrons creates an electric current. Therefore, the chemical energy of the reactants is transformed into electrical energy.

Half-cells

A galvanic cell can be regarded as consisting of two **half-cells**. Each half-cell contains an electrode in contact with a solution (Figure 6.1.7). In the Daniell cell, one half-cell contains Cu(s) and $Cu^{2+}(aq)$; the other contains Zn(s) and $Zn^{2+}(aq)$. The species present in each half-cell form a conjugate redox pair (the oxidised and reduced forms of a substance).

If one member of the conjugate pair in a half-cell is a metal, it is usually used as the electrode. Some redox pairs, such as $Cu^{2+}(aq)/Cu^{+}(aq)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$, do not involve solid metals. If no metal is present, an inert (unreactive) electrode, such as platinum or graphite, is used. This can be seen in Figure 6.1.7.

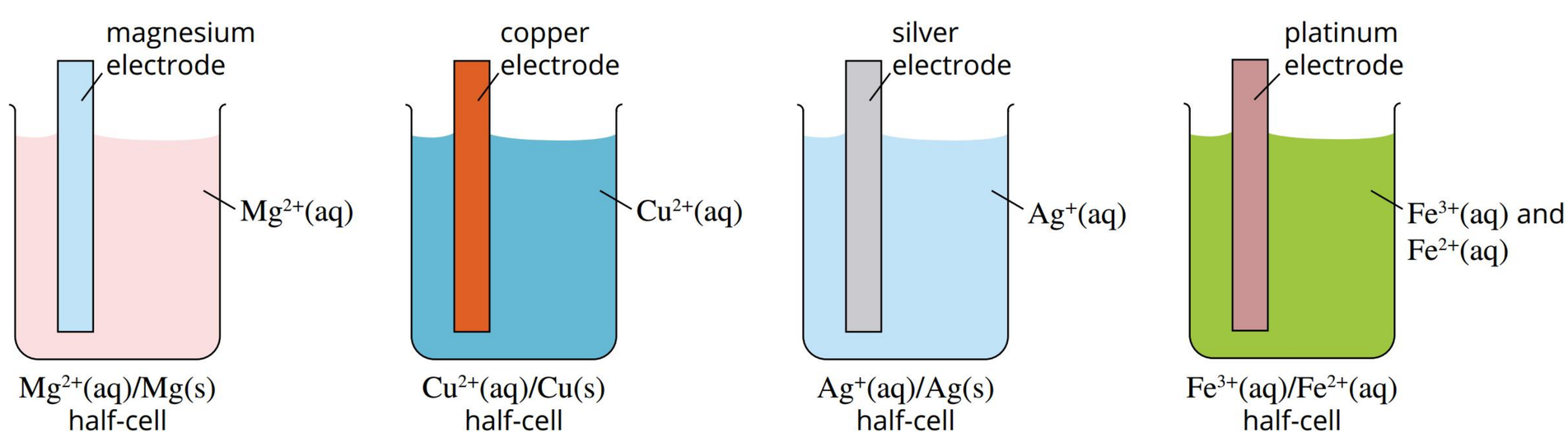


FIGURE 6.1.7 Typical half-cells. The $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell on the right does not contain a solid metal to act as an electrode, so an inert platinum electrode must be added.

In some half-cells, one half of the conjugate pair may be a gas. In such cases, a special 'gas electrode', like the one shown in Figure 6.1.8 for the $H^{+}(aq)/H_2(g)$ half-cell, is used. Note that half-cells usually contain other species not involved in the reaction, such as spectator ions and the solvent.

The electrode at which oxidation occurs is called the anode. In a galvanic cell, the anode, where electrons are released, is described as the negative electrode. The electrode at which reduction occurs is called the cathode. The cathode, where electrons are gained, is the positive electrode in a galvanic cell.

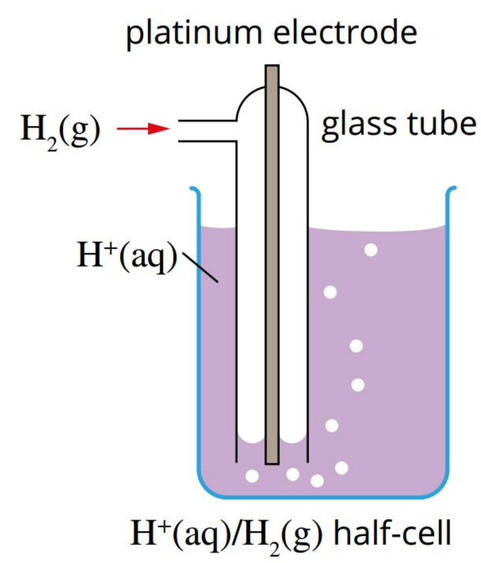


FIGURE 6.1.8 A $H^+(aq)/H_2(g)$ half-cell consists of a platinum rod in a solution of $H^+(aq)$ with H_2 gas bubbling through the solution.

The purpose of the salt bridge

The salt bridge contains soluble ions that are free to move in the presence of an electrical field. The salt bridge therefore completes the electrical circuit and balances charges formed in the two half-cell compartments. *Cat*ions move towards the *cat*hode and *an*ions move towards the *an*ode, as shown in Figure 6.1.9.

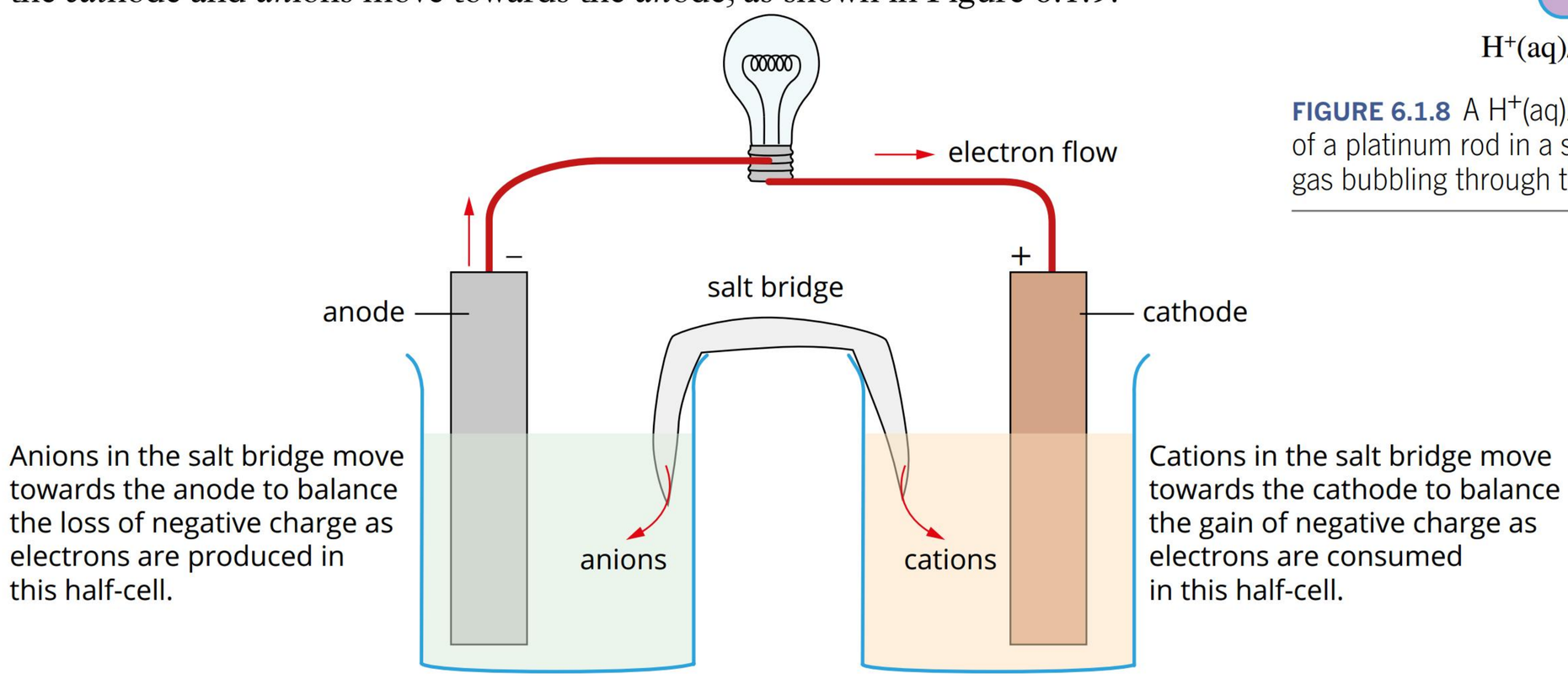


FIGURE 6.1.9 The movement of cations and anions in a salt bridge balances the charges produced and consumed in each half-cell, allowing the flow of electrons through the external circuit.

Without a salt bridge, the solution in one compartment in the galvanic cell would accumulate negative charge and the solution in the other compartment would accumulate positive charge as the reaction proceeded. Such accumulation of charge would stop the reaction very quickly and, hence, prevent further reaction.

Cations in the salt bridge move towards the cathode and anions in the salt bridge move towards the anode.

WRITING HALF-CELL EQUATIONS

If a conjugate redox pair consists of an element and its corresponding ion, then the half-equation is relatively easy to write. For instance, knowing that a reduction reaction involves the conjugate redox pair of Zn^{2+} ions and Zn, you can quickly write the half-cell equation as:

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$

Half-cell equations involving polyatomic ions may be more complex to write. The equation for the reduction reaction in a half-cell containing the dichromate ion ($Cr_2O_7^{2-}$) and Cr^{3+} ion redox pair is:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

You learnt to construct half-equations such as these in Chapter 5.

In balanced half-equations and overall equations, the:

- number of atoms of each element is equal on both sides
- total charge on each side is equal.

Writing an overall equation for a cell reaction

The half-equations for the oxidation and reduction reactions that occur in a cell can be added together to obtain an overall, or full, equation. An overall equation does not show any electrons; all the electrons lost in the oxidation reaction are gained in the reduction reaction. You may need to multiply one or both half-equations by a factor to ensure that the electrons balance and can be cancelled out in the overall equation. Using the equations shown above, zinc will be oxidised by acidified dichromate.

$$(Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-) \times 3$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

The overall equation is:

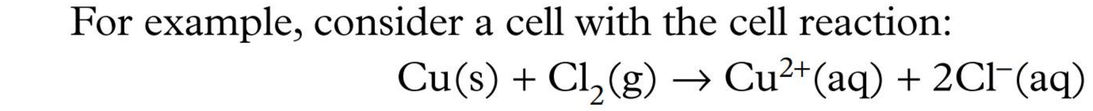
$$3Zn(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

The number of electrons lost in the oxidation reaction must equal the number of electrons gained in the reduction reaction.

DRAWING AND LABELLING A DIAGRAM OF A GALVANIC CELL

If you know the reaction occurring in a galvanic cell, then you can draw a diagram of the cell identifying key features, such as the anode, cathode, electrode polarity, direction of electron flow and direction of the flow of ions.

For example, consider a cell with the cell reaction:



$$Cu(s) + Cl_2(g) \rightarrow Cu^{2+}(aq) + 2Cl^-(aq)$$

From this reaction, you can see that:

- copper metal is at the anode (because copper loses electrons—i.e. copper is oxidised—and oxidation occurs at the anode)
- chlorine gas is at the cathode (because chlorine gains electrons—i.e. chlorine is reduced—and reduction occurs at the cathode).

As in all galvanic cells:

- electrons flow through the external circuit from the anode (negative) to the cathode (positive)
- anions flow in the **internal circuit** to the anode and cations flow towards the cathode.

This information is used to draw and label the diagram of the cell, as shown in Figure 6.1.10.

> To help you remember, try this easy device.
>
> **O**xidation and **A**node both begin with vowels.
>
> **R**eduction and **C**athode both begin with consonants.

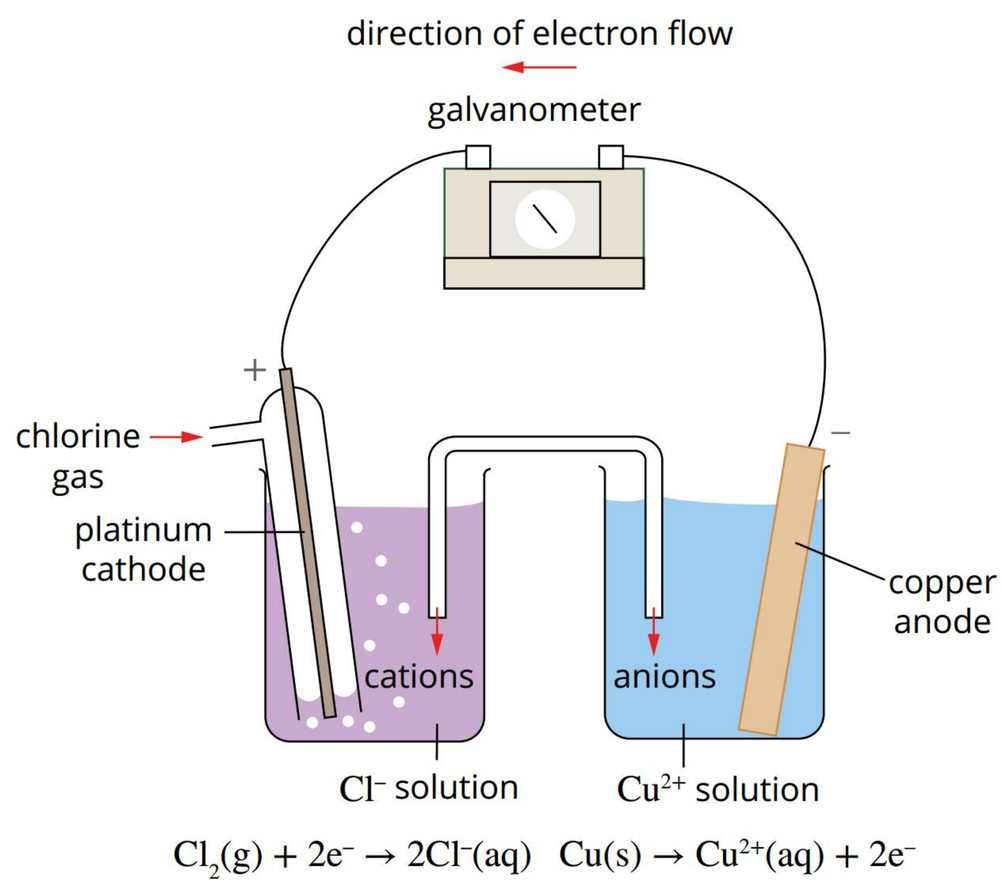


FIGURE 6.1.10 A diagram of the cell containing $Cl_2(g)/Cl^-(aq)$ and $Cu^{2+}(aq)/Cu(s)$ half-cells

6.1 Review

SUMMARY

- Electrochemical cells are devices in which chemical energy is transformed into electrical energy (galvanic cells), or vice versa (electrolytic cells).
- The chemical reactions that occur in galvanic cells are spontaneous and exothermic. The chemical reactions that occur in electrolytic cells are not spontaneous and require electrical energy to create chemical change.
- In a galvanic cell, chemical energy is converted directly into electrical energy via a redox reaction.
- A cell is made from two half-cells.
- Each half-cell contains a conjugate redox pair.
- An oxidation reaction occurs in one half-cell and a reduction reaction occurs in the other half-cell.
- The electrode in the half-cell in which oxidation occurs is called the anode; the electrode in the half-cell in which reduction occurs is called the cathode.
- In galvanic cells, the anode is negative and the cathode is positive.
- Electrons flow through the external circuit from the anode to the cathode.
- A salt bridge completes the electrical circuit in an electrochemical cell and allows a galvanic cell to produce electricity by preventing the accumulation of charge. Cations in the salt bridge move towards the cathode and anions move towards the anode.
- If the reactants in a galvanic cell reaction are allowed to come into direct contact, chemical energy is converted into heat energy rather than electrical energy.
- These key concepts about a galvanic cell are summarised in Figure 6.1.11.

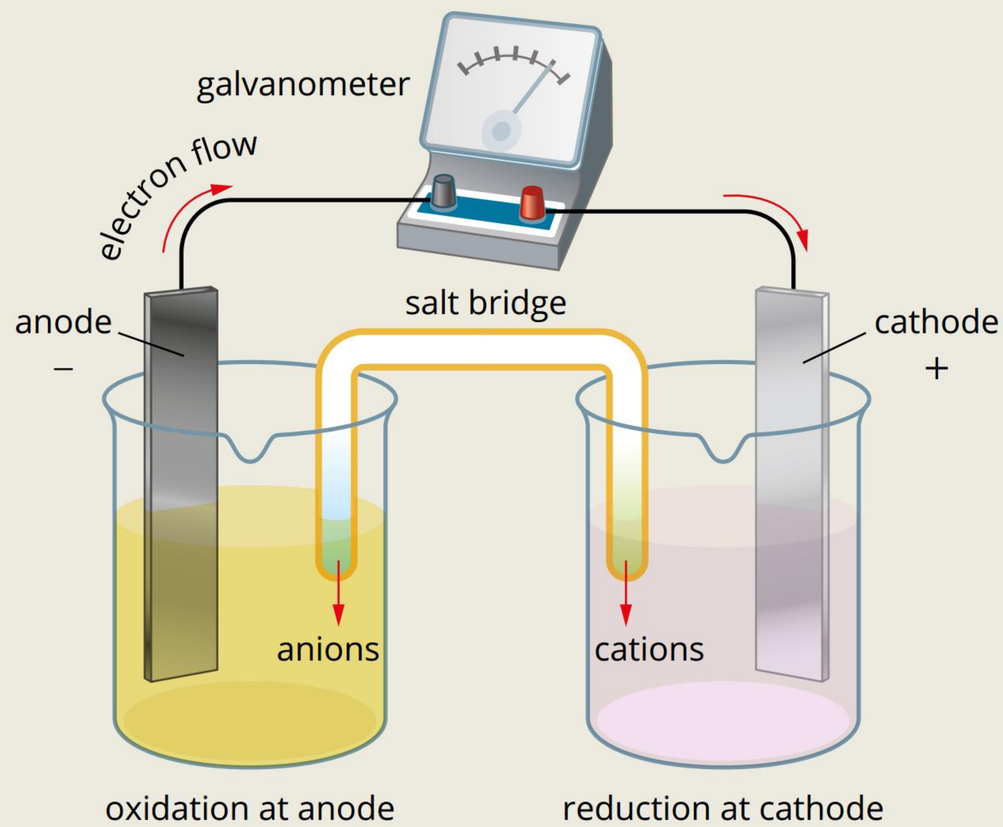


FIGURE 6.1.11 Key concepts about how a galvanic cell works

KEY QUESTIONS

Describe

1 State the meaning of the following terms.

a galvanic cell

b electrochemical cell

c salt bridge

d battery

2 Describe how to construct a galvanic cell.

3 Choose from the correct terms in bold to complete the following sentences correctly.

In a galvanic cell, electrons move through the external circuit from the **positive/negative** electrode to the **positive/negative** electrode. Cations in the salt bridge move towards the **anode/cathode** and anions in the salt bridge move towards the **anode/cathode**.

4 What energy transformation that takes place in:

a a galvanic cell

b an electrolytic cell.

Apply

5 Draw labelled diagrams of the following half-cells.

a $Ni^{2+}(aq)/Ni(s)$

b $Sn^{4+}(aq)/Sn^{2+}(aq)$

c $H^{+}(aq)/H_2(g)$

6 Identify a suitable material to use as the electrode in each of the following half-cells.

a $Mg^{2+}(aq)/Mg(s)$

b $Fe^{3+}(aq)/Fe^{2+}(aq)$

c $Cl_2(g)/Cl^{-}(aq)$

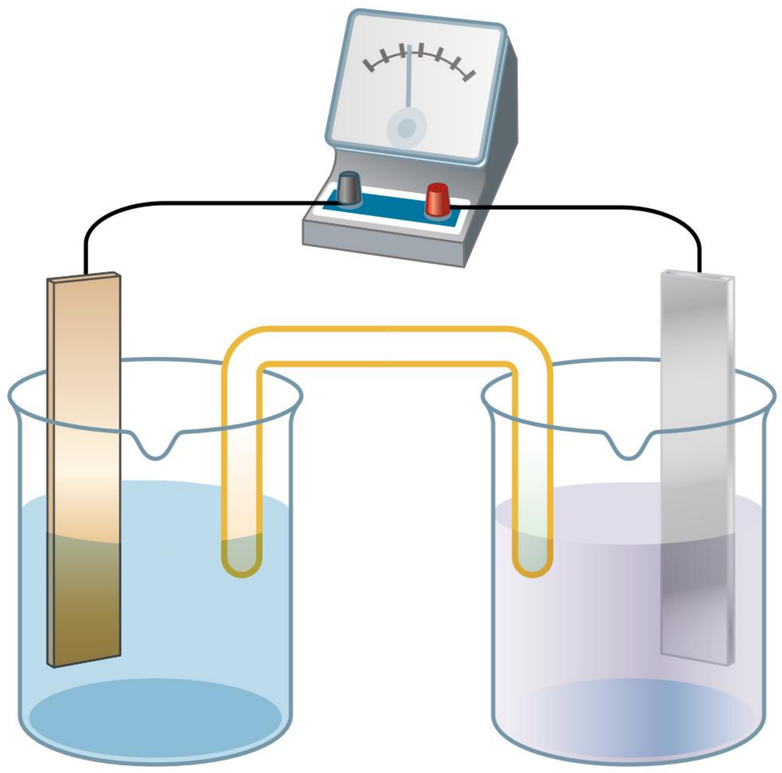
Continued over page

6.1 Review *continued*

7 Label the diagram of the galvanic cell below with the following terms.

- anode
- cathode
- positive electrode
- negative electrode
- reduction reaction
- oxidation reaction
- salt bridge

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$



$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\qquad$ $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

8 In a galvanic cell, the cathode is the positive electrode and the anode is the negative electrode. When a galvanic cell is in operation, the positively charged ions (cations) in the salt bridge move towards the cathode and the negatively charged ions (anions) in the salt bridge move towards the anode. Explain why the cations and anions move in these directions.

9 In a galvanic cell that has the following overall reaction, describe the reactions occurring at the negative and the positive electrodes and the changes that would be observed.

$$Pb^{2+}(aq) + Cd(s) \rightarrow Pb(s) + Cd^{2+}(aq)$$

10 Describe two differences and two similarities between galvanic and electrolytic cells.

Analyse

11 A student prepares a galvanic cell that has the following overall equation:

$$Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$$

a Write the half-equation for the reaction that occurs at the anode.

b Write the half-equation for the reaction that occurs at the cathode.

c The student chooses potassium chloride as the electrolyte for the salt bridge of the cell. Discuss the appropriateness of this choice.

d Explain the purpose of the salt bridge in the function of the cell.

12 The overall equation for the reaction that occurs in a cell made up of $Al^{3+}(aq)/Al(s)$ and $Sn^{2+}(aq)/Sn(s)$ half-cells is:

$$2Al(s) + 3Sn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Sn(s)$$

Write the half-equations for the reaction occurring at the:

a cathode

b anode.

13 Draw a diagram of the cell from question **11** and label the:

- half-equation for the reaction occurring in each half-cell
- anode and cathode
- direction of electron flow
- electrode polarities (which electrode is positive and which is negative)
- direction of anion and cation flow from the salt bridge.

14 The following reaction occurs within a galvanic cell:

$$Mg(s) + Cl_2(g) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

a Identify the half-cell that acts as the:

i anode of the cell

ii cathode of the cell.

b Compare the energy change that occurs in the cell with the energy change that occurs when magnesium and chlorine react directly.

15 A galvanic cell is constructed from $Sn^{4+}(aq)/Sn^{2+}(aq)$ and $H^+(aq)/H_2(g)$ half-cells. If the $Sn^{4+}(aq)/Sn^{2+}(aq)$ half-cell is positive, determine the:

a half-cell that acts as the anode

b direction of movement of cations in the salt bridge

c overall equation for the cell reaction.

6.2 The standard electrode potential, E^o

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- describe the standard hydrogen electrode
- explain standard electrode (reduction) potentials
- use standard electrode potentials to predict the reactions that will occur in different cells under standard conditions, including calculating their cell potentials
- understand that the relative strength of oxidising and reducing agents can be compared using standard electrode potentials.

In Chapter 5, you learnt that redox reactions involve oxidation (where one substance loses electrons) and reduction (where another substance gains electrons). In the previous module, you saw that galvanic cells involve redox reactions where the oxidation and reduction processes are physically separated into different compartments, which we call half-cells. For example, in the Daniell cell (Figure 6.2.1), oxidation occurs at the zinc electrode, where zinc atoms are oxidised to Zn^{2+} ions

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

and reduction occurs at the cathode, where copper(II) ions are reduced to copper metal.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

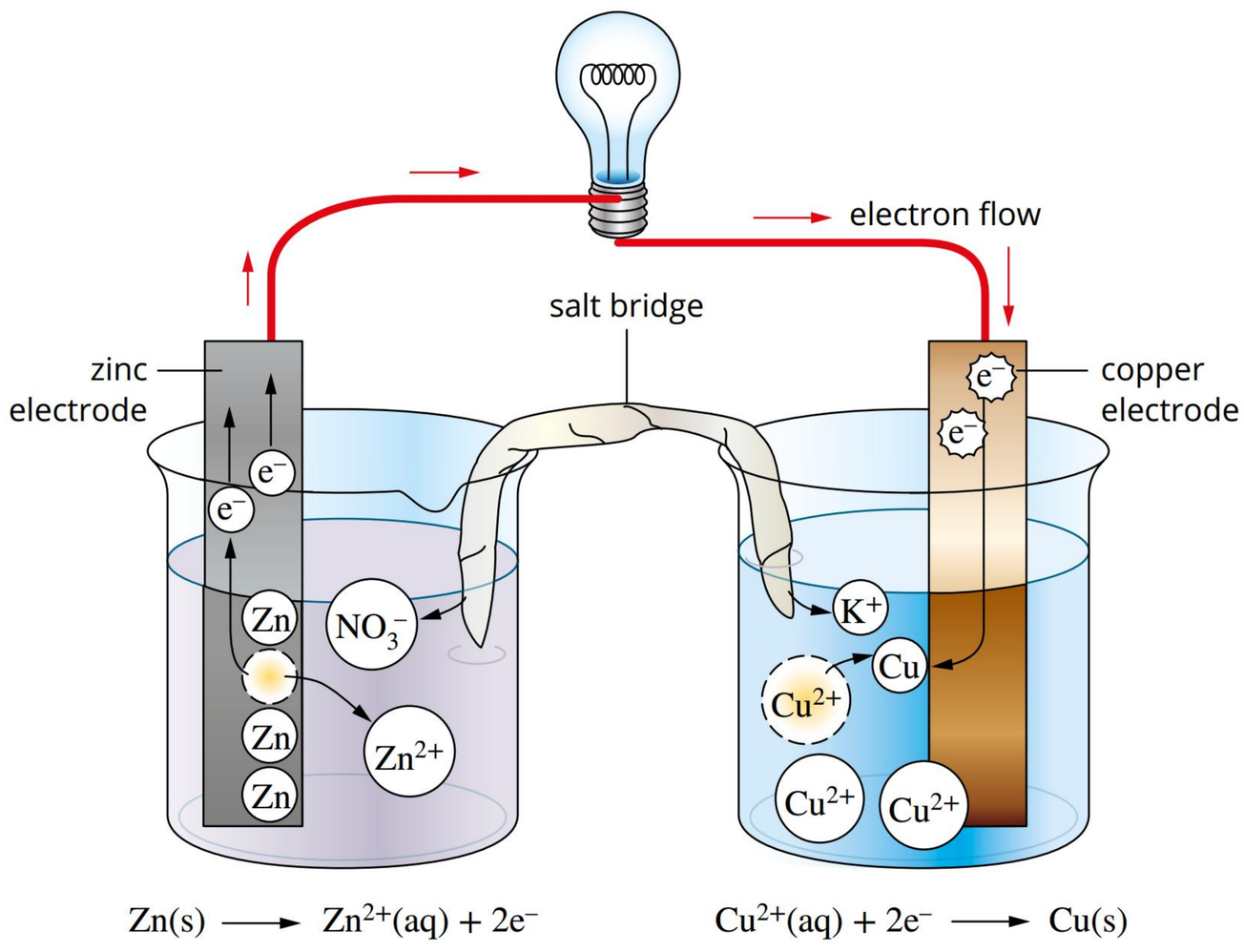


FIGURE 6.2.1 A representation of the electrode reactions in a Daniell cell. The salt bridge contains potassium nitrate solution.

Separating the oxidation and reduction processes into two half-cells offers several advantages for understanding and applying redox reactions. For example, it helps you to:

- predict the products of various reactions by understanding which substances are likely to be oxidised or reduced under given conditions
- predict the spontaneity of cell reactions and direct redox reactions

- calculate the voltage of a galvanic cell, critical for battery and energy storage applications
- assess the relative strengths of oxidising and reducing agents.

POTENTIAL DIFFERENCE, EMF AND STANDARD ELECTRODE POTENTIALS

A current flows in a galvanic cell because one half-cell has a greater tendency to spontaneously push electrons into the external circuit compared to the other half-cell. In the Daniell cell (Figure 6.2.1), the valence electrons of zinc atoms in the anode have a higher energy than the valence electrons of atoms in the copper cathode. As a result, electrons will flow spontaneously from the zinc metal, through the external circuit, to the Cu^{2+} ions at the surface of the copper cathode in the other half-cell compartment.

This is analogous to water flowing downhill from a position of high potential energy to a position of low potential energy. And just as flowing water can be made to do work by turning a waterwheel, the energy of electron flow (from high potential energy to low potential energy) can be used to do work, such as lighting a globe or powering an electric vehicle.

In galvanic cells, we say that a **potential difference** exists between the two half-cells. This potential difference is sometimes called the **electromotive force**, or emf, and is commonly referred to as the cell voltage. It is the potential difference between the two half-cells in a galvanic cell that drives electron flow in the external circuit.

The potential difference of an electrochemical cell is typically given the symbol *E*, in historical reference to the term emf. The SI unit for potential difference (and emf) is the **volt**, which has the symbol V. In practice, the potential difference (or emf) between two compartments of a galvanic cell is measured with a **voltmeter**.

Potential differences of cells are usually reported under the **standard conditions** of:

- a pressure of 100 kPa (1 atm)
- 1 mol L^{-1} concentration of solutions
- a fixed temperature of 25°C (or 298 K).

The potential difference of a cell under standard conditions is given the symbol $E°$.

Standard hydrogen electrode

It is impossible to measure the potential difference of an isolated half-cell because both oxidation and reduction must take place for a potential difference to exist. However, you can assign a standard half-cell potential ($E°$) to each half-cell by connecting the cells to a standard reference half-cell and measuring the voltage produced.

A hydrogen half-cell, $H^+(aq)/H_2(g)$, under standard conditions, is used for this purpose and its $E°$ value is arbitrarily assigned a value of zero. This half-cell is known as the **standard hydrogen half-cell** or the standard hydrogen electrode (SHE). The SHE is the standard reference electrode used to measure the electrode potentials of other half-cells. Figure 6.2.2 shows the $H^+(aq)/H_2(g)$ half-cell made from a platinum electrode placed in acid solution with hydrogen gas bubbled over it. The pressure of the hydrogen gas is 100 kPa (1 bar), the hydrogen ion concentration is 1.0 mol L^{-1} and the temperature is 298 K (25°C). The $E°$ value of the SHE is assigned 0.00 volts when measured under standard conditions. A salt bridge is used to connect the SHE to another half-cell to allow measurement of the overall potential difference of the full galvanic cell, as shown in Figure 6.2.3.

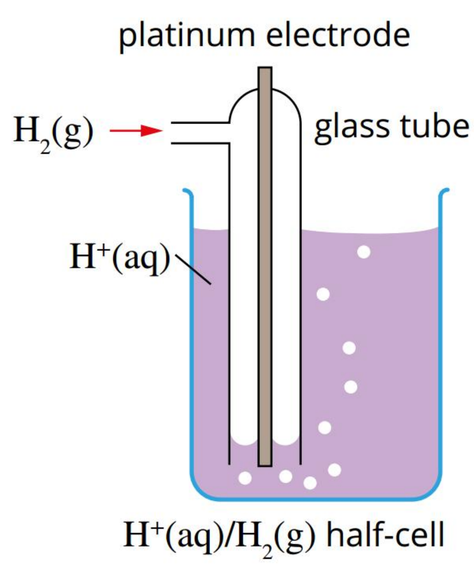


FIGURE 6.2.2 A $H^+(aq)/H_2(g)$ half-cell consists of a platinum rod in a solution of $H^+(aq)$ with H_2 gas bubbling through the solution.

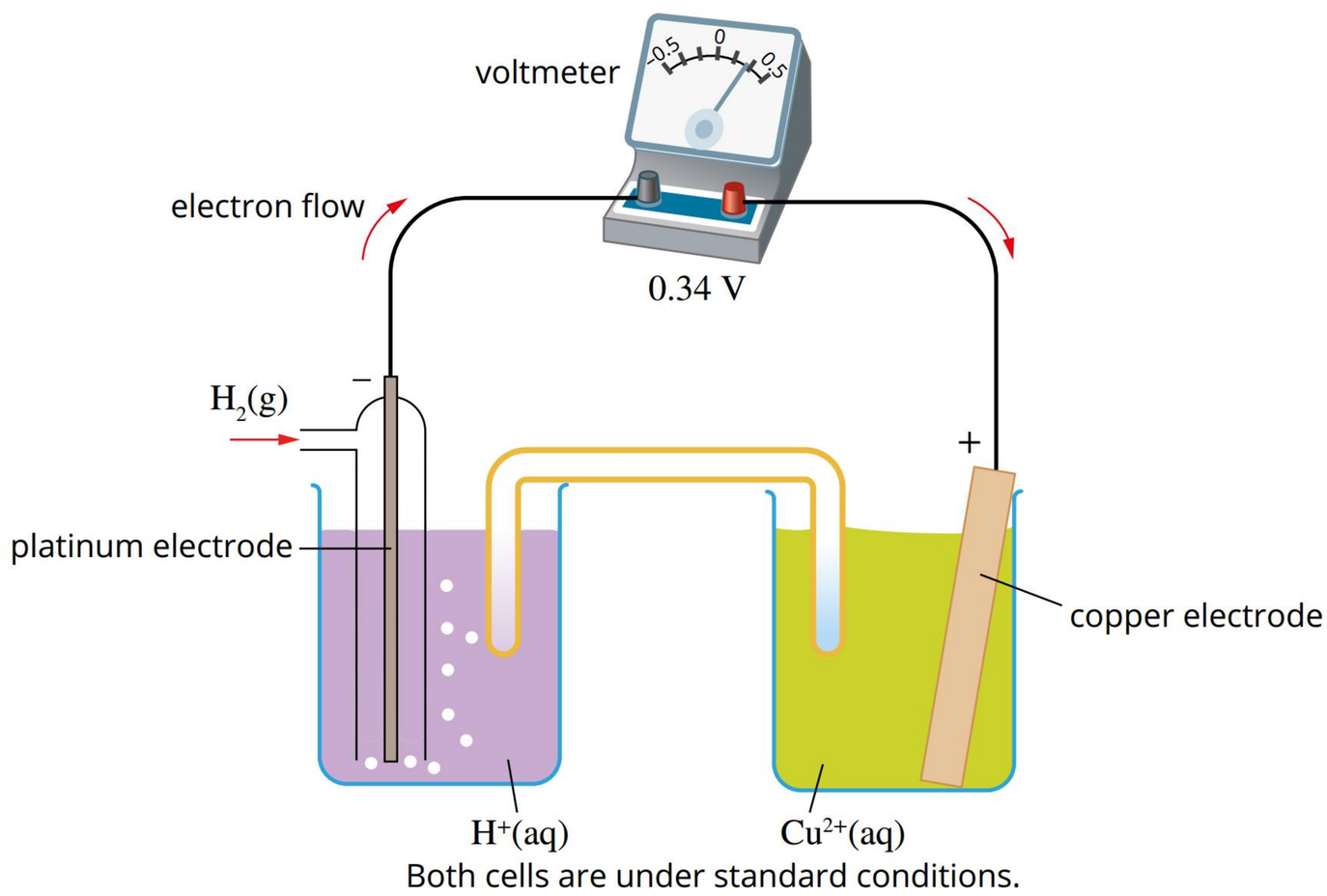


FIGURE 6.2.3 Measuring the standard half-cell potential of a $Cu^{2+}(aq)/Cu(s)$ half-cell. From the voltmeter reading, the $E°$ of this half-cell is 0.34 V.

Standard electrode potentials

The value of 0.34 V in Figure 6.2.3 is known as both the **standard electrode potential** and the **standard reduction potential**, and is given the symbol $E°$. By connecting the standard hydrogen electrode to different half-cells and measuring their cell potentials, chemists have developed a long list of standard reduction potentials (see Table 6.2.1 on page 195 and Table 2 in Appendix E). Notice the value of 0.00 V given for the $H^+(aq)/H_2(g)$ half-equation. All other $E°$ values are measured relative to this arbitrary value.

It is important to understand that the standard electrode potential gives a numerical measure of the tendency of a half-cell reaction to occur *as a reduction reaction*. For example, a positive value of $E° = 0.34$ V for the $Cu^{2+}(aq)/Cu(s)$ half-cell indicates that when connected to the SHE, the reaction in this half-cell will proceed as a reduction process. The reduction half-equation can be written as the forward reaction shown in Table 6.2.1, i.e.:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

In this case, the copper electrode operates as a cathode (where reduction takes place) and is designated the positive electrode (Figure 6.2.3).

The other electrode in this galvanic cell, the SHE, will therefore operate as an anode (where oxidation takes place) and is designated the negative electrode. The oxidation half-equation can be written as the reverse reaction shown in Table 6.2.1 (page 195), i.e.:

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

with the overall cell redox reaction being represented as:

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$$

By contrast, Table 6.2.1 shows a negative value of $E°$ for the $Fe^{2+}(aq)/Fe(s)$ half-cell (i.e. $E° = -0.44$ V). This means that this half-cell has a lower tendency to occur as a reduction reaction when coupled with the SHE. Figure 6.2.4 shows the same experimental set-up as in Figure 6.2.3 except the copper, Cu(s), electrode has been replaced by an iron, Fe(s), electrode.

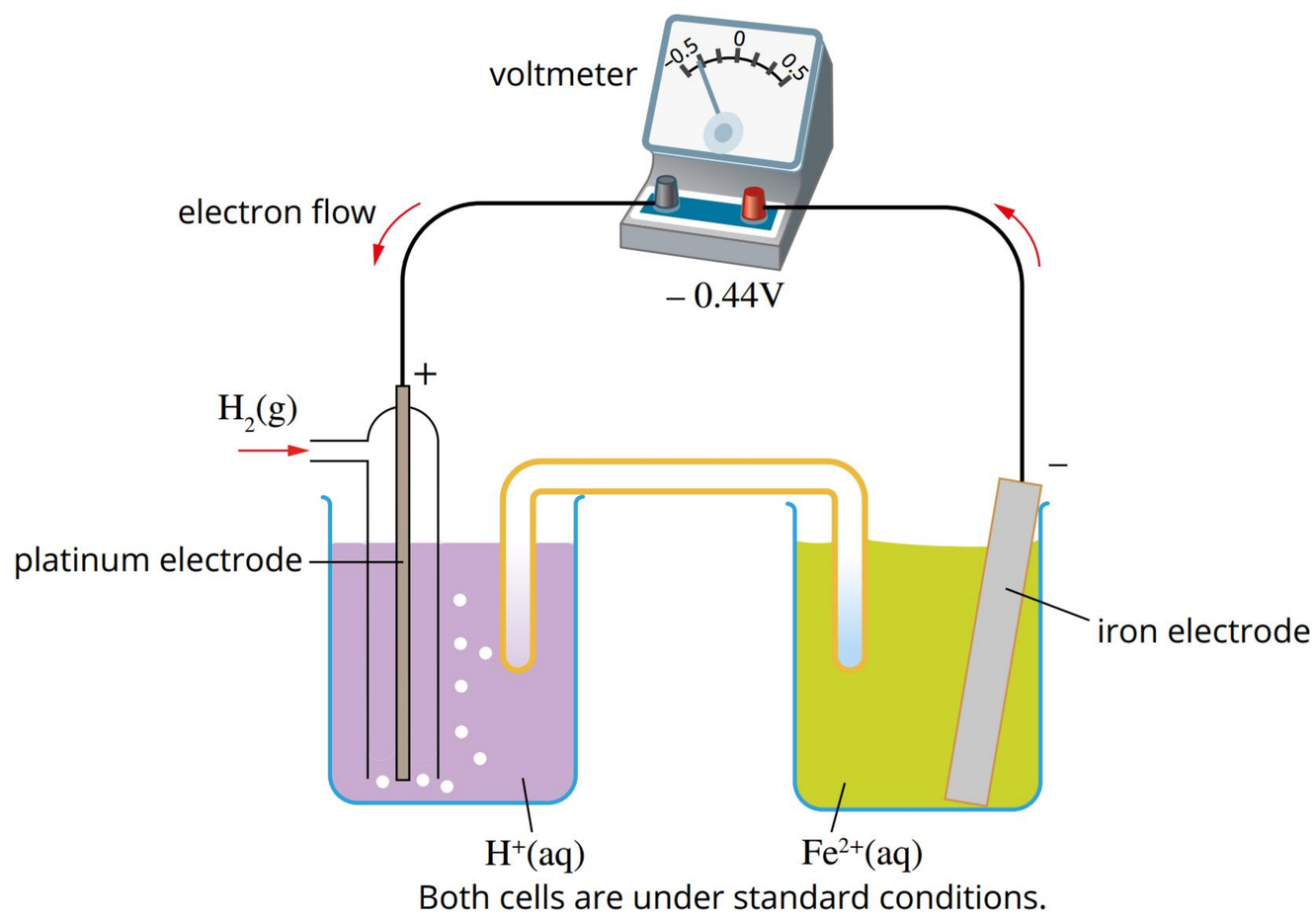


FIGURE 6.2.4 Measuring the standard half-cell potential of a $Fe^{2+}(aq)/Fe(s)$ half-cell. From the voltmeter reading and the negative polarity of the iron electrode, the E^o of this half-cell is –0.44 V.

Here, you see the electron flow goes in the opposite direction, with the iron electrode operating as the anode with an oxidation process occurring. The half-equation is therefore written as the reverse of the process shown in Table 6.2.1 on page 195, i.e.:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

The iron electrode undergoes oxidation because (relative to the SHE) the $Fe^{2+}(aq)/Fe(s)$ half-cell has a lower tendency to occur as a reduction, as evidenced by the negative E^o value. In this case, therefore, the SHE operates as a cathode with the reduction half-equation written as shown in Table 6.2.1:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

The overall cell reaction being represented as:

$$Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$$

You can see from the above that standard electrode potentials can be used to predict how two half-cells will function when coupled together to form a galvanic cell. *In general, the half-cell with the more positive E° value will occur as a reduction process*; its electrode will be the cathode and will have a positive sign. The other half-cell in the coupled galvanic cell will occur as an oxidation process; its electrode will be the anode, with a negative sign.

A final word about the standard electrode potentials shown in Table 6.2.1: they are measured under standard conditions where solutions are at 25°C and have a concentration of 1.0 mol L^{-1}, and gases are at 25°C with a pressure of 100 kPa (1 bar). Under non-standard conditions, the values of E^o in Table 6.2.1 may change.

When two cell half-cells are coupled, the cell with the most positive E° value will operate as a reduction process and the other cell will operate as an oxidation process.

TABLE 6.2.1 The standard electrode (reduction) potential for common redox conjugate pairs. The table is organised so that the strongest oxidising agents are at the bottom left of the table (e.g. $F_2(g)$) and the strongest reducing agents are at the top right of the table (e.g. Li(s)). All standard electrode potentials are measured under standard conditions.

Strength as an oxidising agent	Oxidised species ⇌ reduced species	E° (volts)	Strength as a reducing agent
very weak oxidising agents	$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.04	very strong reducing agents
	$K^+(aq) + e^- \rightleftharpoons K(s)$	–2.94	
	$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	–2.91	
	$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	–2.87	
	$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.71	
	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.36	
	$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	–1.68	
	$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	–1.18	
	$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	–0.83	
	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76	
	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44	
	$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.24	
	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	–0.14	
	$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	–0.13	
increasing strength as oxidising agents	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00	increasing strength as reducing agents
	$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15	
	$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.16	
	$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons SO_2(aq) + 2H_2O(l)$	+0.16	
	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34	
	$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40	
	$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+0.52	
	$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54	
	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77	
	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80	
	$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.08	
	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23	
	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51	
very strong oxidising agents	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.89	very weak reducing agents

Using the standard electrode potentials

The data shown in Table 6.2.1 are the result of the work of many scientists. This table is one of the most useful references for chemists. Two uses of this table are described below.

Predicting cell reactions

As you saw above, you can use the standard electrode potentials to predict what will happen when two specific half-cells are combined to form a cell. To do this, remember that the half-reaction with the more positive E° value goes in the forward direction and the half-equation is written as a reduction process (with electrons on the LHS of the arrows); the other half-reaction is reversed and is written as an oxidation process (with electrons on the RHS of the arrow).

Another way to predict the cell reactions that will occur is to remember that the strongest oxidising agent in the cell will react with the strongest reducing agent. As a consequence:

- a reduction reaction will occur in the half-cell with the more positive $E°$ value, whereas an oxidation reaction will occur in the other half-cell with the more negative $E°$ value
- the positive electrode (cathode) will be in the half-cell with the more positive $E°$ value, whereas the negative electrode (anode) will be in the other half-cell.

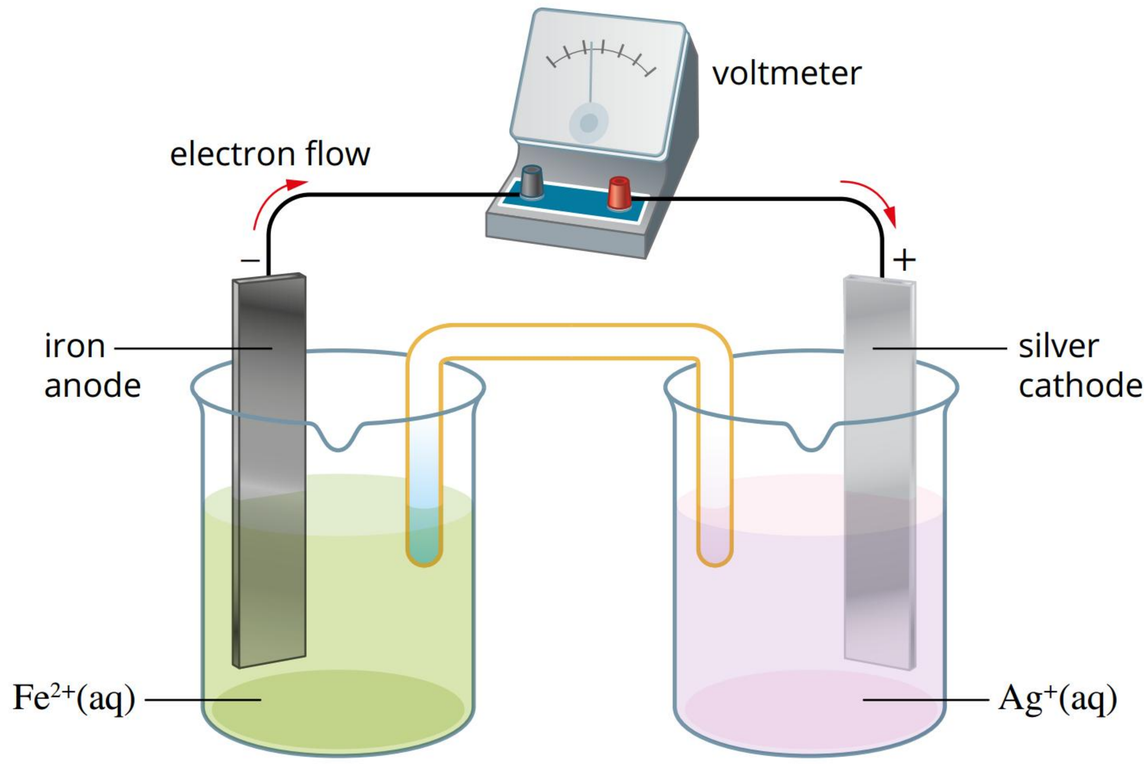
The equation for the overall cell reaction is found by adding the two half-equations. Worked example 6.2.1 shows how to use the electrochemical series to predict a cell reaction.

Worked example 6.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL

A galvanic cell is made from $Ag^+(aq)/Ag(s)$ and $Fe^{2+}(aq)/Fe(s)$ half-cells under standard conditions and at 25°C. Use the standard electrode potential values to predict the overall cell reaction, identify the anode and cathode, and determine the direction of electron flow.

Thinking	Working
Identify the two relevant half-equations from the list of standard electrode potentials.	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ $E° = -0.44\,V$ $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $E° = +0.80\,V$
Identify the half-equation with the most positive $E°$ value. This half-equation will occur as a reduction process and will be the reduction half-cell. The other half-equation will occur as an oxidation process and will be the oxidation half-cell.	The $Ag^+(aq)/Ag(s)$ half-cell has the most positive $E°$ value and will therefore be the reduction half-cell. Its half-equation will be written as a reduction process. The $Fe^{2+}(aq)/Fe(s)$ half-cell has the most negative $E°$ value and will therefore be the oxidation half-cell. Its half-equation will be written as an oxidation process.
Construct the two half-equations that will occur. (Hint: The strongest oxidising agent will react with the strongest reducing agent; or as noted above, the reduction process has the most positive $E°$ value and the oxidation process has the most negative $E°$ value).	Reduction: $Ag^+(aq) + e^- \rightarrow Ag(s)$ Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ Since this is the oxidation process, the equation from Table 6.2.1 on page 195 should be written in reverse.
Construct the overall cell equation.	Multiply the $Ag^+(aq)/Ag(s)$ half-cell equation by 2 so that the number of electrons in each half-equation is equal, and then add the two equations together: $[Ag^+(aq) + e^- \rightarrow Ag(s)] \times 2$ $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ $2Ag^+(aq) + Fe(s) \rightarrow 2Ag(s) + Fe^{2+}(aq)$
Identify the anode and cathode in this cell. The anode is the electrode at which oxidation occurs. The cathode is the electrode at which reduction occurs.	The iron electrode will be the anode and the silver electrode will be the cathode.

Determine the polarities of the electrodes and the direction of electron flow in the cell. The anode is negative; the cathode is positive.	Electrons flow from the negative iron electrode (anode) to the positive silver electrode (cathode), as shown in Figure 6.2.5.  **FIGURE 6.2.5** A diagram of the cell containing $Fe^{2+}(aq)/Fe(s)$ and $Ag^{+}(aq)/Ag(s)$ half-cells

➤ Try yourself 6.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL

A galvanic cell is made from $Sn^{2+}(aq)/Sn(s)$ and $Ni^{2+}(aq)/Ni(s)$ half-cells under standard conditions and at 25°C. Use the standard electrode potential values to predict the overall cell reaction, identify the anode and cathode, and determine the direction of electron flow.

Calculating the voltage of a cell

The maximum potential difference of a cell under standard conditions is the difference between the $E°$ values of its two half-cells. It is defined as follows:

cell potential difference = $E°$ of reduction half-cell – $E°$ of oxidation half-cell

An easy way to remember this for galvanic cells is:

cell potential difference = more positive half-cell $E°$ – less positive half-cell $E°$

For example, the maximum cell voltage of a cell constructed from $Ag^{+}(aq)/Ag(s)$ and $Fe^{2+}(aq)/Fe(s)$ half-cells under standard conditions can be calculated as follows:

cell potential difference = more positive half-cell $E°$ – less positive half-cell $E°$

$$= E°(Ag^{+}(aq)/Ag(s)) - E°(Fe^{2+}(aq)/Fe(s))$$
$$= +0.80 - (-0.44)$$
$$= 1.24\,V$$

Different values for the cell voltage are obtained under non-standard conditions.

As a galvanic cell discharges, the cell voltage eventually drops to zero and the cell is referred to as 'flat'.

> **i** The easiest way to calculate the cell potential difference is to remember:
>
> cell potential difference = more positive half-cell $E°$ – less positive half-cell $E°$

Worked example 6.2.2

CALCULATING THE VOLTAGE OF A GALVANIC CELL

Calculate the maximum cell voltage of a cell made from $Mg^{2+}(aq)/Mg(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cells under standard conditions and at 25°C.	
Thinking	**Working**
Identify the two relevant half-equations from the list of standard electrode potentials (Table 6.2.1 on page 195).	$Mg^{2+}(aq) + 2e^{-} \rightleftharpoons Mg(s)$ $E° = -2.36$ V $Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$ $E° = +0.77$ V

Identify which half-cell is the reduction half-cell (noting that the other half-cell will be the oxidation half-cell) and then calculate the cell potential using the formula: $E^{o}_{cell} = E^{o}_{(reduction)} - E^{o}_{(oxidation)}$	The reduction process will occur in the half-cell with the more positive E^{o} value, i.e.: The $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell is the reduction half-cell because it has $E^{\circ} = +0.77$ V compared to $E^{\circ} = -2.36$ V for the $Mg^{2+}(aq)/Mg(s)$ half-cell. $E^{o}_{cell} = E^{o}_{(reduction)} - E^{o}_{(oxidation)}$ $E^{o}_{cell} = +0.77 - (-2.36) = 3.13$ V
Alternatively, you could use the following relationship: cell potential difference = more positive half-cell E° – less positive half–cell E°	Alternatively, E^{o}_{cell} = more positive half-cell E° – less positive half-cell E° $E^{o}_{cell} = +0.77 - (-2.36) = 3.13$ V

➤ Try yourself 6.2.2

CALCULATING THE VOLTAGE OF A GALVANIC CELL

Calculate the maximum cell voltage of a cell made from $Cl_2(g)/Cl^-(aq)$ and $Br_2(l)/Br^-(aq)$ half-cells under standard conditions and at 25°C.

Assessing the relative strength of oxidising and reducing agents

The list of standard electrode potentials in Table 6.2.1 on page 195 is structured so that the strongest oxidising agent, $F_2(g)$, is at the bottom left of the table and the strongest reducing agent, Li(s), is at the top right of the table. In a galvanic cell, the stronger oxidising agent in the cell will react with the stronger reducing agent. The stronger oxidising agent is reduced, so it is in the half-cell with the cathode (the positive electrode). By contrast, the stronger reducing agent is oxidised, so it is in the half-cell with the anode (the negative electrode).

Table 6.2.1 can therefore be used to assess the relative strengths of oxidising and reducing agents. Oxidising agents are themselves reduced in redox reactions. You can therefore identify the oxidising agents in Table 6.2.1 as those chemical species on the left-hand side of the arrows, whose oxidation numbers decrease going from left to right in the half-equations. These include:

- the strong oxidising agents such as F_2, H_2O_2, MnO_4^- and $Cr_2O_7^{2-}$
- the very weak oxidising agents such as Li^+, K^+, Ba^{2+} and Ca^{2+}
- intermediate-strength oxidising agents such as Fe^{3+}, I_2 and Cu^{2+}.

By contrast, reducing agents are themselves oxidised in redox reactions, and you can identify them as those chemical species on the right-hand side of the arrows, whose oxidation numbers increase going from right to left in the half-equations. These include:

- the strong reducing agents such as Li, K and Ba
- the very weak reducing agents such as F^-, H_2O, Mn^{2+} and Cr^{3+}
- intermediate-strength reducing agents such as Zn, Fe, Ni and Sn.

You will also note from these examples that the conjugate redox partner of a strong oxidising agent (e.g. F_2) is a weak reducing agent (i.e. F^-). Conversely, the conjugate redox partner of a strong reducing agent (e.g. Li) is a weak oxidising agent (i.e. Li^+).

Worked example 6.2.3

DETERMINING THE RELATIVE STRENGTH OF OXIDISING AND REDUCING AGENTS

Determine which of the following halogens is the strongest oxidising agent: chlorine (Cl_2), bromine (Br_2) and iodine (I_2).

Thinking	Working
Identify the relevant half-equations from the list of standard electrode potentials (Table 6.2.1 on page 195).	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E° = +1.36$ V $Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$ $E° = +1.08$ V $I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ $E° = +0.54$ V
The half-equation with the highest reduction potential ($E°$) value will be the strongest oxidising agent—chlorine (Cl_2).	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E° = +1.36$ V

➤ Try yourself 6.2.3

DETERMINING THE RELATIVE STRENGTH OF OXIDISING AND REDUCING AGENTS

Determine which of the following alkali metals is the strongest reducing agent: sodium (Na), lithium (Li) and potassium (K).

Strong reducing agents donate electrons more readily than weak ones.

Strong oxidising agents accept electrons more readily than weak ones.

Strong reducing agents have weak conjugate oxidising agents.

Strong oxidising agents have weak conjugate reducing agents.

6.2 Review

SUMMARY

- The standard hydrogen electrode (SHE) is used as the standard reference half-cell. When it is used under standard conditions, its E° value is arbitrarily assigned as zero.
- The standard electrode potential or standard reduction potential (E°) of a half-cell is measured by connecting the half-cell to a standard hydrogen half-cell and measuring the voltage produced under standard conditions.
- The standard electrode potential gives a numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction.
- Relatively positive E° values indicate that the half-cell has a high tendency to undergo reduction processes; relatively negative E° values indicate that the half-cell has a high tendency to undergo oxidation processes.
- In the table of standard electrode potentials, half-reactions are often listed in order so that the strongest oxidising agent is at the bottom left of the table (with the most positive E° value) and the strongest reducing agent is at the top right (with the most negative E° value)—as in Table 6.2.1 on page 195 and Table 2 in Appendix E.
- Standard electrode potentials are valid under standard conditions; that is, gas pressures of 100 kPa (1 bar) and solution concentrations of 1.0 mol L^{-1}. Standard electrode potentials are usually measured at 25°C (298 K).
- The relative strengths of oxidising and reducing agents can be determined by comparing standard electrode potentials, and these can be used to predict half-cell and overall cell reactions.
- The maximum potential difference of a cell under standard conditions (E°_{cell}) can be calculated from standard electrode potentials:

  cell potential difference, E°_{cell} = E° of reduction half-cell – E° of oxidation half-cell

  or, more simply:

  cell potential difference = more positive half-cell E° – less positive half-cell E°.

KEY QUESTIONS

Describe

1 State the meaning of the following terms.

a potential difference

b standard conditions

c standard electrode potential

2 Choose from the terms in bold to complete the following sentences correctly.

In a galvanic cell, the stronger reducing agent is in the half-cell with the **negative/positive** electrode. This electrode is the **anode/cathode**. The stronger oxidising agent is in the half-cell with the **negative/positive** electrode. This electrode is the **anode/cathode**.

3 From the list of metals below, select the metal which is the strongest reducing agent.

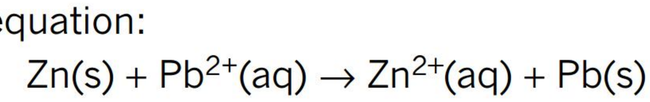
zinc magnesium nickel lead

Apply

4 Describe how the standard electrode potential (E°) of a half-cell is measured using a standard hydrogen electrode. In your answer, describe how the sign of the electrode potential is determined.

5 Describe what would happen if the lithium half-cell had been chosen as the standard reference electrode (assigned 0 volts) instead of the hydrogen half-cell.

6 A student sets up a galvanic cell with the following overall equation:



$$Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$$

The voltmeter records a voltage of 0.38 V, yet the laboratory manual states the E° for the cell should read 0.63 V. Identify potential reasons for the discrepancy between the value obtained and the laboratory manual.

Analyse

7 A galvanic cell was constructed from $Al^{3+}(aq)/Al(s)$ and $Pb^{2+}(aq)/Pb(s)$ half-cells. Use standard electrode potentials (Table 2 in Appendix E) to predict the:

- **a** oxidation and reduction half-equations
- **b** overall cell reaction
- **c** identity of the anode and cathode.

8 Draw a diagram of a cell formed from $Cl_2(g)/Cl^-(aq)$ and $Sn^{2+}(aq)/Sn(s)$ half-cells. Using standard electrode potentials (Table 2 in Appendix E), label the diagram to show the:

- **a** half-cell reactions
- **b** anode and cathode
- **c** direction of electron flow
- **d** electrode polarities (which electrode is positive and which is negative)
- **e** directions of flow of the anions and cations in the salt bridge
- **f** overall reaction.

9 For the following half-cells

- **i** $Fe^{3+}(aq)/Fe^{2+}(aq)$ and $H^+(aq)/H_2(g)$
- **ii** $Cl_2(g)/Cl^-(aq)$ and $Pb^{2+}(aq)/Pb(s)$

use standard electrode potentials (Table 2 in Appendix E) to predict the:

- **a** half-cell reactions
- **b** anode and cathode
- **c** direction of electron flow
- **d** electrode polarities (which electrode is positive and which is negative)
- **e** directions of flow of the anions and cations in the salt bridge
- **f** overall reaction.

10 Calculate the potential difference for cells constructed from the following standard half-cells.

- **a** $Ag^+(aq)/Ag(aq)$ and $H^+(aq)/H_2(g)$
- **b** $Br_2(l)/Br^-(aq)$ and $Fe^{2+}(aq)/Fe(s)$

11 A standard cell has the following cell reaction:

$$2H^+(aq) + 2Cr^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + H_2(g)$$

If the potential difference (E^o_{cell}) of this cell is +0.40 V, determine the E^o for the following half-reaction:

$$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$$

12 A cell constructed from standard $Ti^{3+}(aq)/Ti^{2+}(aq)$ and $Br_2(l)/Br^-(aq)$ half-cells has a potential difference of 1.46 V. If the electrode in the $Ti^{3+}(aq)/Ti^{2+}(aq)$ half-cell is negative, use the standard electrode values (Table 2 in Appendix E) to calculate the standard electrode potential of a $Ti^{3+}(aq)/Ti^{2+}(aq)$ half-cell.

13 A cell is constructed from standard $Ni^{2+}(aq)/Ni(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cells.

- **a** Identify the strongest oxidising agent in the cell.
- **b** Identify the strongest reducing agent in the cell.
- **c** Describe the direction of flow of cations and anions in the salt bridge.

14 Consider the galvanic cells made from standard half-cells as listed below. Rank the cells in order of their voltage, from highest to lowest.

$Ag^+(aq)/Ag(s)$ and $Cl_2(g)/Cl^-(aq)$
$Fe^{2+}(aq)/Fe(s)$ and $Ag^+(aq)/Ag(s)$
$Fe^{2+}(aq)/Fe(s)$ and $Cl_2(g)/Cl^-(aq)$

6.3 Predicting direct redox reactions

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- predict whether a redox reaction will occur when chemicals are directly mixed
- recognise the limitations associated with the use of standard reduction potentials to predict whether a redox reaction will be observed.

The table of standard electrode (reduction) potentials (Table 6.2.1 on page 195) provides us with a ranking of the relative strengths of oxidising and reducing agents.

In this module, you will see that you can apply your understanding of Table 6.2.1 to predict the likelihood of a redox reaction taking place when different chemicals are combined.

PREDICTING REACTIONS

If the contents of the half-cells of a galvanic cell were mixed, the reactants would react directly. Energy would be released as heat rather than as electrical energy. For example, if the components reacting in the Daniell cell (the zinc metal and the copper ion solution) are allowed to come into direct contact, they will react as shown in Figure 6.1.5 (page 186). Reactions that occur in galvanic cells or when chemicals are directly mixed are described as naturally occurring reactions, or spontaneous reactions.

In the last module, you saw that in a galvanic cell, the strongest oxidising agent in the cell reacts with the strongest reducing agent. In other words, the half-reaction with the more positive $E°$ value in Table 6.2.1 occurs in the forward direction (as reduction), and the reaction with the more negative $E°$ value occurs in the reverse direction (as oxidation).

This principle applies equally to redox reactions that occur when reactants are mixed directly. You will recall in Chapter 5 that metal displacement reactions were discussed. A more reactive metal will be oxidised by, and donate its electrons to, the cation of a less reactive metal. The cation that receives the electrons is reduced. For a spontaneous redox reaction to occur, the metal ions of one metal must be below the other metal in the reactivity series discussed in Chapter 5.

As shown in Figure 6.3.1, for a spontaneous reaction to occur, an oxidising agent (on the left of Table 6.2.1) must react with a reducing agent (on the right) that has a more negative $E°$ value. Because this is the case when zinc metal is placed in a copper ion solution, a spontaneous reaction occurs. The same will not occur when copper metal is placed in a solution of zinc ions.

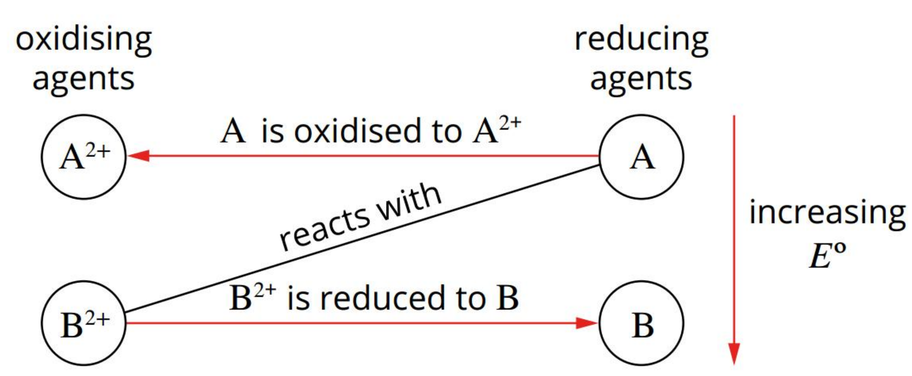


FIGURE 6.3.1 Oxidising agents only react significantly with reducing agents that have more negative $E°$ values.

With half-equations arranged in order of increasing oxidising agent strength (as in Table 6.2.1), you can predict that a spontaneous reaction will occur by looking for substances that are arranged in a top-right/bottom-left position.

Worked example 6.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following reduction equations that appear in the order shown in Table 6.2.1 on page 195.

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \qquad E^\circ = -2.36\ V$$
$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \qquad E^\circ = -0.24\ V$$
$$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq) \qquad E^\circ = +1.08\ V$$

Use Table 6.2.1 and the standard electrode potential values to predict the effect of mixing:

a $Br_2(l)$ and $Mg^{2+}(aq)$

b $Mg^{2+}(aq)$ and $Ni(s)$

c $Ni^{2+}(aq)$ and $Mg(s)$.

Thinking	Working
Identify the two relevant half-equations from the table of standard electrode potential values (Table 6.2.1). Predict whether a reaction occurs. A chemical species on the left of the table (an oxidising agent) reacts with a chemical species on the right (a reducing agent) that has a half-reaction with a more negative E° value. Construct the overall equation.	**a** $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $E^\circ = -2.36\,V$ $Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$ $E^\circ = +1.08\,V$ No reaction occurs because both $Br_2(aq)$ and $Mg^{2+}(aq)$ are oxidising agents. **b** $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $E^\circ = -2.36\,V$ $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E^\circ = -0.24\,V$ No reaction occurs because the half–reaction involving the oxidising agent, Mg^{2+}, has a more negative E° than that of the reducing agent, Ni, in Table 6.2.1. **c** $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $E^\circ = -2.36\,V$ $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E^\circ = -0.24\,V$ A reaction occurs because the half-reaction involving the oxidising agent, Ni^{2+}, has a more positive E° than that of the reducing agent, Mg, in Table 6.2.1. The lower half-equation in Table 6.2.1 occurs in the forward direction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ The higher half-equation occurs in the reverse direction: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ The overall reaction equation is found by adding the half-equations: $Ni^{2+}(aq) + Mg(s) \rightarrow Ni(s) + Mg^{2+}(aq)$

➤ Try yourself 6.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following reduction equations that appear in the order shown in Table 6.2.1 on page 195.

$$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s) \qquad E^\circ = -0.13\,V$$
$$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq) \qquad E^\circ = +0.54\,V$$
$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^\circ = +1.36\,V$$

Use Table 6.2.1 and the standard electrode potential values to predict the effect of mixing:

a $I_2(s)$ and $Pb^{2+}(aq)$

b $Cl^-(aq)$ and $I_2(s)$

c $I_2(s)$ and $Pb(s)$.

Limitations of predictions

The standard half-cell potentials given in Table 6.2.1 on page 195 are measured under standard conditions (i.e. solutions are 1.0 mol L^{-1} in concentration, gases are at a pressure of 100 kPa and the operating temperature of the cell is 298 K). As you would expect, half-cell potentials can vary under other conditions.

When conditions are very different from standard conditions, the order of half-reactions in Table 6.2.1 may also be different, and predictions of reactions based on the standard half-cell potentials may not be reliable. In real-world applications, experimental conditions often deviate from the standard conditions, which can result in different measured cell potentials. There are also unwanted side reactions at electrode surfaces in real-world applications that can affect the measurements taken.

It is also important to remember that the standard electrode potential values give no information about the rate at which reactions occur. The standard electrode potentials are measured under equilibrium conditions, and they do not provide information about the reaction kinetics or the rate of reaction. A cell reaction may have a positive $E°$ value and therefore be predicted to be spontaneous, yet it might occur at a very slow rate and therefore be perceived as not proceeding spontaneously. This could be due to a high activation energy or other factors. Two common examples of this include:

1. the conversion of the diamond allotrope of carbon to its more stable graphite form:

   $$C_{diamond} \rightarrow C_{graphite}$$

   The process has a very high activation energy due to the strong covalent bonds in diamond, making this transformation a very slow process under normal, everyday conditions of temperature and pressure.
2. The rusting (or oxidation) of iron, which can be represented simplistically by the following chemical equation:

   $$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

   This reaction occurs slowly because it requires specific environmental conditions (e.g. the presence of moisture, oxygen and electrolytes) and therefore does not occur instantly to any significant extent, even in the presence of air and water.

6.3 Review

SUMMARY

- The relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials, and these can be used to predict the tendency of a reaction to occur, both in galvanic cells and direct reactions.
- For a spontaneous reaction to occur, an oxidising agent (on the left of Table 6.2.1 on page 195) must react with a reducing agent (on the right) that has a more negative $E°$ value.
- Overall equations for redox reactions can be obtained by adding half-equations.
- When reactants react in a galvanic cell, chemical energy is transformed into electrical energy. However, when they react directly, their chemical energy is transformed into heat energy.
- Standard half-cell potentials are measured under standard conditions. Under other conditions, predictions based on standard electrode potential values may not be reliable.
- Standard electrode potential values give no information about the rate at which reactions may occur.

KEY QUESTIONS

Describe

1. Describe the conditions necessary for an oxidising agent to react with a reducing agent under standard conditions when the reactants are mixed directly.
2. Choose from the terms in bold to complete the following sentences correctly.

   The standard electrode (reduction) potentials are used to determine $E°$ values and are measured under **standard/non-standard conditions**. A **positive/negative** $E°_{cell}$ value is required for a reaction to occur spontaneously. This value is a **guarantee/guide** that a reaction is possible. The $E°$ value **does/does not** provide any information about the reaction rate.

Apply

3 Explain why predictions of reactions based on the standard half-cell potentials do not always correspond with observations when the reactants are mixed.

4 Use the standard electrode (reduction) potential values (Table 2 in Appendix E) to determine whether:

- **a** sodium is a stronger reducing agent than lithium
- **b** $Fe^{2+}(aq)$ is a stronger oxidising agent than $Ca^{2+}(aq)$
- **c** $Sn^{2+}(aq)$ can act as an oxidising agent and a reducing agent.

5 When protecting iron from corrosion, metals such as magnesium and zinc are used as sacrificial anodes. Write the oxidation half-equations for iron, zinc and magnesium and use the standard electrode (reduction) potential values (Table 2 in Appendix E) to illustrate that zinc and magnesium are fit for the purpose of protecting iron.

6 Using the standard electrode (reduction) potential values, a student identifies that the following metals should react with 1 mol L^{-1} H^+ ion:

lead iron zinc magnesium

- **a** Explain how the student could use the standard electrode (reduction) potential values to draw this conclusion.
- **b** When the student performs an experiment, they find that only zinc and magnesium produce a visible reaction. Explain this observation.

Analyse

7 Use the table of standard electrode (reduction) potential values (Table 2 in Appendix E) to determine whether a reaction will occur when the following are mixed.

- **a** $Cl_2(g)$ and $Fe^{2+}(aq)$
- **b** $Br^-(aq)$ and $I_2(s)$
- **c** $Br^-(aq)$ and $Zn(s)$
- **d** $Fe^{2+}(aq)$ and $Zn(s)$

8 Using the table of standard electrode (reduction) potential values (Table 2 in Appendix E), determine whether a reaction will occur in the following situations. If a reaction does occur, construct the overall equation for the reaction.

- **a** Chlorine gas is bubbled into a solution containing bromide ions.
- **b** Chlorine gas is bubbled into a solution containing iodide ions.
- **c** A bromine solution is added to a solution containing chloride ions.
- **d** A bromine solution is added to a solution containing iodide ions.

9 Iron nails are placed into 1 mol L^{-1} solutions of $CuSO_4$, $MgCl_2$, $Pb(NO_3)_2$ and $ZnCl_2$. Use the table of standard electrode (reduction) potential values (Table 2 in Appendix E) to identify in which solution(s) you would expect a coating of a metal other than iron to appear on the nail.

10 Carbon reduction is a method of purifying metals from their metal ores. A spontaneous reaction is essential in this process and not all metals can be purified in this manner. The half-equation for CO_2/CO is shown below:

$$CO_2 + 2H_2O + 2e \rightarrow CO + 2OH^- \quad E° = -0.934\ V$$

Examine the table of standard electrode (reduction) potential values (Table 2 in Appendix E), and predict which metals will be able to be purified by this carbon reduction process. Justify your choice with an explanation.

11 Silver jewellery can be cleaned very effectively with aluminium foil. The jewellery is sprinkled with table salt and placed in a piece of foil that will completely enclose it, with sufficient hot water to dampen it. The half-equation for the silver reaction is:

$$Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}(aq) \quad E° = -0.934\ V$$

- **a** Write the half-equation for the aluminium reaction.
- **b** Write the overall equation for the process.
- **c** What is the cell potential for this reaction?
- **d** What is the purpose of the salt in the reaction taking place?

Chapter review

06

KEY TERMS

battery
electrochemical cell
electrode
electrolyte
electrolytic cell
electromotive force
external circuit
galvanic cell
galvanometer
half-cell
internal circuit
potential difference
salt bridge
spontaneous reaction
standard conditions
standard electrode potential
standard hydrogen half-cell
standard reduction potential
volt
voltmeter

KEY QUESTIONS

Describe

1 Identify which one of the following statements best describes the role of the salt bridge in a galvanic cell.

A It provides a pathway for electrons to move between the half-cells.

B It allows the movement of ions to balance charges formed at the electrodes.

C It allows reactants from one half-cell to mix with reactants from the other half-cell.

D It allows positive charges to accumulate in one half-cell and negative charges to accumulate in the other.

2 Identify which one of the following statements about a galvanic cell is correct.

A The electrode where oxidation occurs is the cathode.

B Electrons flow towards the electrode where oxidation occurs.

C The electrode where oxidation occurs has a negative polarity.

D Anions flow into the half-cell containing the electrode where reduction occurs.

3 **a** Name the half-cell that is used as the reference for the measurement of standard electrode potential (E^o).

b Indicate the meaning of the term 'standard conditions'.

4 When comparing the characteristics of galvanic and electrolytic cells, which one of the following is incorrect?

	Galvanic	Electrolytic
A	produce electrical energy	consume electrical energy
B	involve a non-spontaneous reaction	involve a spontaneous reaction
C	oxidation occurs at the anode	oxidation occurs at the anode
D	anode is negative	anode is positive

5 Choose from the terms in bold to complete the following sentences correctly.

Galvanic cells **produce/consume** electrical energy. They do this by undergoing a **spontaneous/non-spontaneous** reaction. The anode is the site of **reduction/oxidation** in all cells. Electrons move in the **internal/external** circuit.

Apply

6 Identify which one of the following materials would be least suitable for use as an electrode in a $Cl_2(g)/Cl^-(aq)$ half-cell.

A iron

B gold

C graphite

D platinum

7 Identify which one of the following statements about the oxidising and reducing agents in a galvanic cell is correct.

A The stronger oxidising agent is in the half-cell that acts as the anode.

B The stronger reducing agent is in the half-cell that acts as the cathode.

C The stronger reducing agent is in the half-cell with the negative electrode.

D The stronger oxidising agent is in the half-cell with the negative electrode.

8 Identify which one of the following metals you would expect to be coated with nickel when immersed in a solution of nickel(II) nitrate.

A tin

B zinc

C silver

D copper

9 Explain how the table of standard electrode (reduction) potential values can be used to identify the relative strengths of oxidising and reducing agents.

10 Choose from the terms in bold to correctly complete the following sentences.

A spontaneous redox reaction will occur if an oxidising agent (on the **left/right** of Table 6.2.1 on page 195) reacts with a reducing agent (on the **left/right** of Table 6.2.1) that has a half-reaction with **more/less** positive E° value. **Electrical/heat** energy is released.

11 The overall reaction for a galvanic cell constructed from the $Cl_2(g)/Cl^-(aq)$ and $Pb^{2+}(aq)/Pb(s)$ half-cells is:

$$Cl_2(g) + Pb(s) \rightarrow 2Cl^-(aq) + Pb^{2+}(aq)$$

Draw a diagram of the galvanic cell and on your diagram show the:

a direction of electron flow in the external circuit
b half-equation for the reaction at each electrode
c anode
d positive electrode
e direction of cation flow in the salt bridge.

12 Two half-cells are set up. One contains a solution of magnesium nitrate with a strip of magnesium as the electrode. The other contains lead nitrate with a strip of lead as the electrode. The solutions in the two half-cells are connected by a piece of filter paper soaked in potassium nitrate solution. When the electrodes are connected by wires to a galvanometer, the magnesium electrode is shown to be negatively charged.

a Sketch the galvanic cell described. Label the positive and negative electrodes. Mark the direction of the electron flow.
b Construct the half-equations for the reactions that occur in each half-cell and an equation for the overall reaction.
c Label the anode and cathode.
d Indicate the direction in which ions in the salt bridge migrate.

13 Show that under standard conditions, according to the table of standard electrode (reduction) potential values (Table 2 in Appendix E), the Daniell cell (Figure 6.1.3 on page 184) should have a cell potential difference of 1.10 V.

14 Each of these pairs of half-cells combines to form a galvanic cell.

i $Ag^+(aq)/Ag(s)$ and $Zn^{2+}(aq)/Zn(s)$
ii $Fe^{2+}(aq)/Fe(s)$ and $Pb^{2+}(aq)/Pb(s)$
iii $Ni^{2+}(aq)/Ni(s)$ and $Cu^{2+}(aq)/Cu(s)$

Draw a diagram of each galvanic cell and on your diagrams show the:

a direction of electron flow in the external circuit
b half-equation for the reaction at each electrode
c equation for the overall reaction in the galvanic cell
d anode
e positive electrode
f direction negative ions flow in the salt bridge.

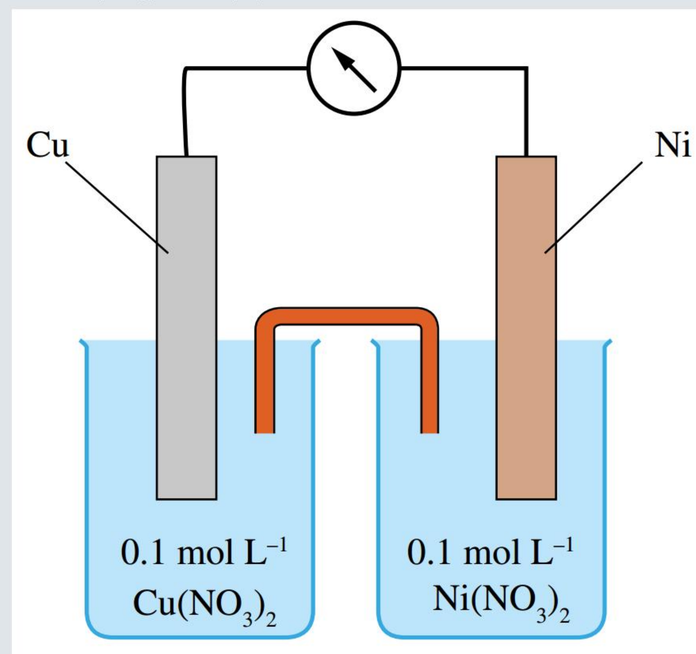
15 Explain the difference between:

a an anode and a cathode
b a cell and a battery.

16 Use the table of standard electrode (reduction) potential values (Table 2 in Appendix E) to determine whether:

a elemental iodine is an oxidising agent or a reducing agent
b calcium metal is a strong or weak reducing agent
c nickel is a better reducing agent than silver
d $Cu^{2+}(aq)$ is a better oxidising agent than $Ag^+(aq)$
e $Fe^{2+}(aq)$ can act as an oxidising agent and a reducing agent.

17 A galvanic cell is constructed from $Ni^{2+}(aq)/Ni(s)$ and $Cu^{2+}(aq)/Cu(s)$ half-cells as shown below.



a Label the anode and cathode on the diagram.
b Write the oxidation and reduction half-cell equations and the overall equation for the cell.
c Explain why the standard electrode potentials cannot be used to determine the E° value of this cell.

18 The standard hydrogen electrode contains a platinum electrode.

a What is the purpose of the platinum electrode in the standard hydrogen electrode?
b Could the platinum electrode be replaced with another material and what features should this material have?

19 Galvanic cells containing silver oxide are commonly used in watches. Below are the two half-equations for the reactions taking place in a silver oxide cell.

$$Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$$
$$Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$$

Identify the incorrect statement about this cell.

A Zinc is acting as the anode in the cell.
B Silver oxide is being reduced as the cell operates.
C Electrons move from the anode to the cathode through the internal circuit.
D The cell is an example of an alkaline cell.

20 A copper electrode is placed in each of the 1 mol L^{-1} ionic solutions listed below. In which one would you observe a visible reaction?

A zinc nitrate
B lead(II) nitrate
C magnesium nitrate
D silver nitrate

Analyse

21 The E° for the half-equation:
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$ is +0.17 V. Which one of the following species would react with $H_2S(aq)$ but not with $H_2O(l)$ under standard conditions.

A $Cl_2(g)$
B Cu(s)
C Mg(s)
D $Ag^+(aq)$

22 Consider the following two half-equations and their standard electrode potentials.

$$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s) \quad E^\circ = -0.14\ V$$
$$Be^{2+}(aq) + 2e^- \rightleftharpoons Be(s) \quad E^\circ = -1.85\ V$$

Determine which one of the following is the strongest oxidising agent.

A Sn(s)
B Be(s)
C $Sn^{2+}(aq)$
D $Be^{2+}(aq)$

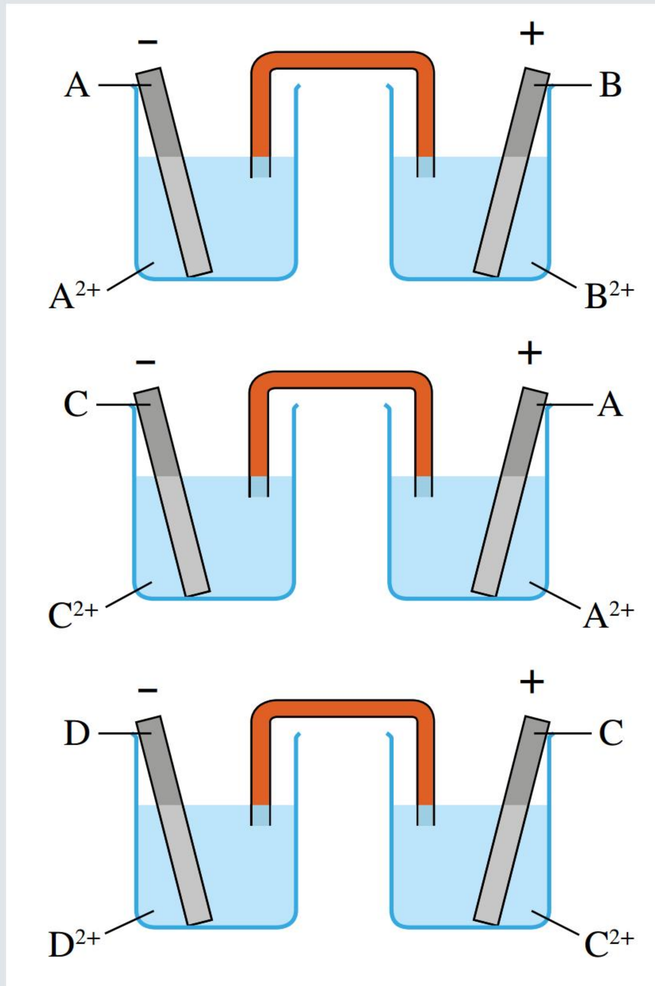
23 A cell is constructed from $Pb^{2+}(aq)/Pb(s)$ and $Ni^{2+}(aq)/Ni(s)$ half-cells. If the $Ni^{2+}(aq)/Ni(s)$ half-cell is negative, deduce the:

a half-cell that acts as the anode
b overall equation for the cell reaction
c strongest oxidising agent in the cell.

24 Consider the four galvanic cells made from half-cells as listed below. Use the standard electrode potential values (Table 2 in Appendix E) to rank the galvanic cells in order of the maximum voltage they could generate under standard conditions.

- $Fe^{2+}(aq)/Fe(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{2+}(aq)/Fe(s)$
- $Ni^{2+}(aq)/Ni(s)$ and $Br_2(l)/Br^-(aq)$
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$

25 Four half-cells, $A^{2+}(aq)/A(s)$, $B^{2+}(aq)/B(s)$, $C^{2+}(aq)/C(s)$ and $D^{2+}(aq)/D(s)$, are used to make the cells shown above and to the right.



Rank the half-cells in increasing order of their reduction half-cell potentials, i.e. from lowest to highest.

26 The following equations appear in the order shown in the table of standard electrode potential values (Table 6.2.1 on page 195):

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$
$$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$$
$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$$

i Predict whether a redox reaction would occur in the following mixtures. Assume concentrations of 1 mol L^{-1} and gas pressures of 100 kPa.

For mixtures where you predict a reaction will occur, construct:

ii separate half-equations for the oxidation and reduction reactions
iii an overall equation.

a $Cl_2(g)$ and Zn(s)
b $Ag^+(aq)$ and Ag(s)
c $Ag^+(aq)$ and Zn(s)
d $Zn^{2+}(aq)$ and $Cl^-(aq)$

27 Use the table of standard electrode (reduction) potential values (Table 2 in Appendix E) to predict whether a reaction will occur in each of the following situations. Construct an equation for each reaction that you predict will occur.

a Copper(II) sulfate solution is stored in an aluminium container.
b Sodium chloride solution is stored in a copper container.
c Silver nitrate solution is stored in a zinc container.

d An iron nail is placed in 1 mol L^{-1} hydrochloric acid solution.

e A plumber uses hydrochloric acid to clean copper pipes.

28 The following equations form part of the table of standard electrode (reduction) potential values. They are ranked in the order shown.

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$$
$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$
$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$$
$$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$$
$$Ag^{+}(aq) + e^- \rightleftharpoons Ag(s)$$

a Determine which species is the strongest oxidising agent and which species is the weakest oxidising agent.

b Determine which species is the strongest reducing agent and which species is the weakest reducing agent.

c Lead rods are placed in solutions of silver nitrate, iron(II) sulfate and magnesium chloride. Determine in which solutions you would expect to see a coating of another metal form on the lead rod. Explain.

d Determine which of the metals silver, zinc or magnesium might be coated with lead when immersed in a solution of lead(II) nitrate.

29 **a** Use the table of standard electrode (reduction) potential values to predict what might be expected to occur if hydrogen gas were bubbled through a solution containing Fe^{3+} ions.

b Construct an equation for the predicted reaction.

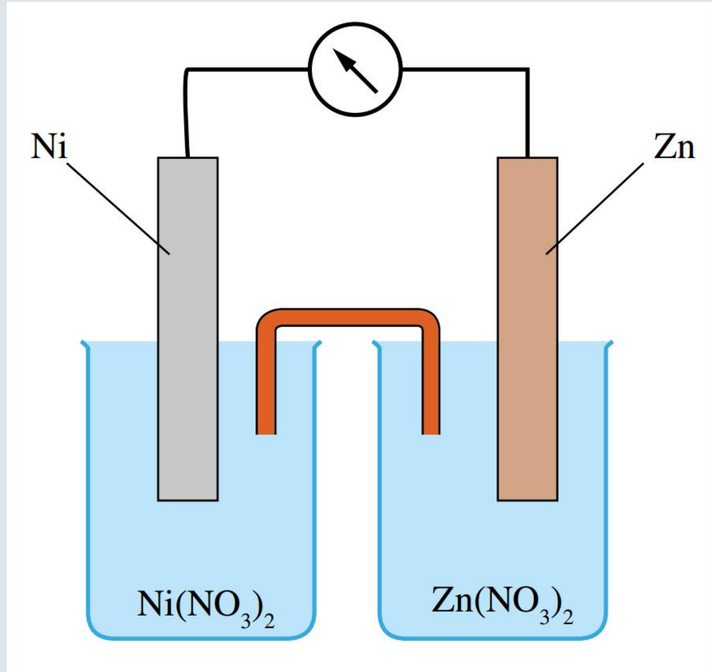
c When the reactants were mixed in an experiment, no reaction was observed. Suggest possible reasons for this.

d Describe the limitations that need to be considered when using standard electrode (reduction) potential values to predict whether a certain reaction will occur.

30 **a** Briefly explain the difference between an electrochemical cell and a galvanic cell.

b Identify a significant difference between a galvanic cell and an electrolytic cell.

31 A laboratory technician is asked to set up the following galvanic cell:



a What is the oxidising agent in the cell?

b What is the reducing agent in the cell?

c The technician cannot find a nickel electrode and uses copper. Will this affect how the cell works? Explain your answer.

Interpret

32 A student was given the following three half-cells:

$$Mn^{2+}(aq)/Mn(s)$$
$$Fe^{2+}(aq)/Fe(s)$$
$$Al^{3+}(aq)/Al(s)$$

Explain how the student could experimentally determine the relative positions of the three redox pairs in the table of standard electrode potential values.

33 Explain the following observations.

a Bromine reacts with iodide ions in solution but does not react with chloride ions.

b Tin metal is added to solutions of tin(II) chloride to prevent oxidation of the tin(II) ions by oxygen in the air.

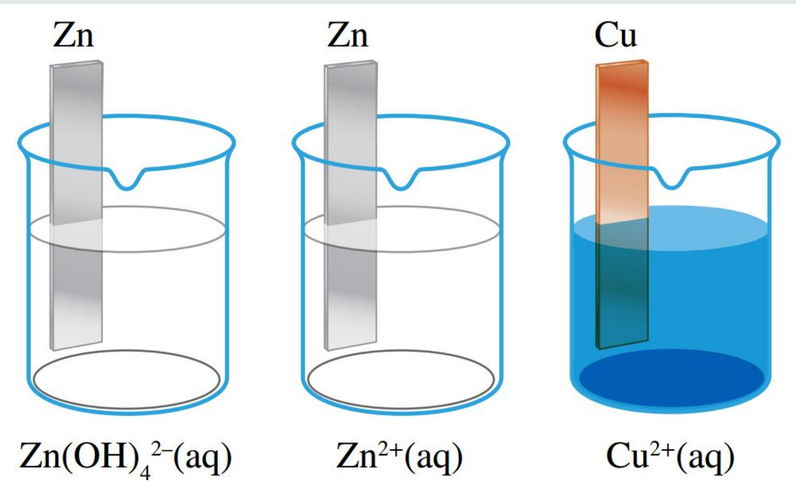
c Blocks of zinc are attached to the iron hulls of ships to reduce corrosion.

34 A student working in the laboratory spilled an iodine solution over the bench, causing a dark brown stain to form. Suggest how the student could remove the iodine stain.

35 Many of the 'alkaline cells' on the market contain zinc electrodes in contact with an electrolyte containing hydroxide ions. The half-cell reaction can be represented as:

$$Zn(s) + 4OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2e^-$$

To investigate whether the standard electrode potential ($E°$) of these half-cells is the same as that of a half-cell reaction using a zinc electrode in contact with a zinc nitrate electrolyte (for which the electrode reaction would be $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$), a student was provided with the two zinc half-cells and $Cu^{2+}(aq)/Cu(s)$ half-cell shown below.



a Construct a net equation for the reaction in a galvanic cell in which the 'alkaline zinc half-cell' is connected to the $Cu^{2+}(aq)/Cu(s)$ half-cell.

b Carefully explain how the student could use the half-cells that were provided to determine whether the two different half-cells containing zinc had the same $E°$ value. Include fully labelled diagrams with your answer and explain how the results could be interpreted.

36 You are given the following materials to investigate electrochemical cells:

- copper, silver and nickel metal strips
- 1 mol L^{-1} solutions of copper(II) nitrate, silver nitrate and nickel(II) nitrate
- a voltmeter
- electrical leads
- strips of filter paper
- saturated solutions of sodium nitrate and potassium chloride.

a Determine which combination of materials will produce the highest cell potential and draw a diagram of this cell. Label the electrodes and the solutions used.

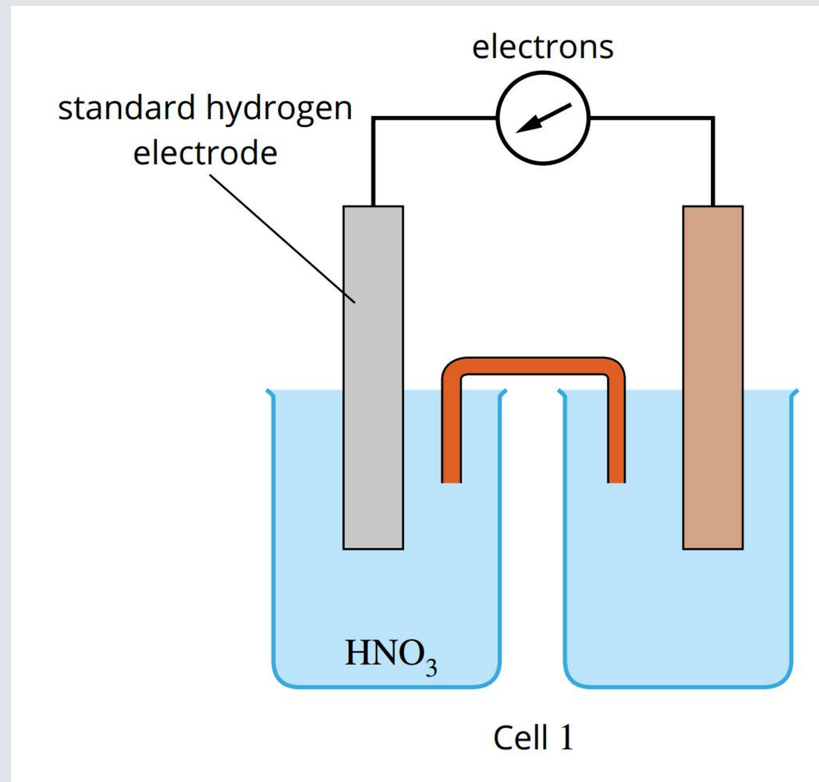
b Write the half-equations for the cell and the overall equation.

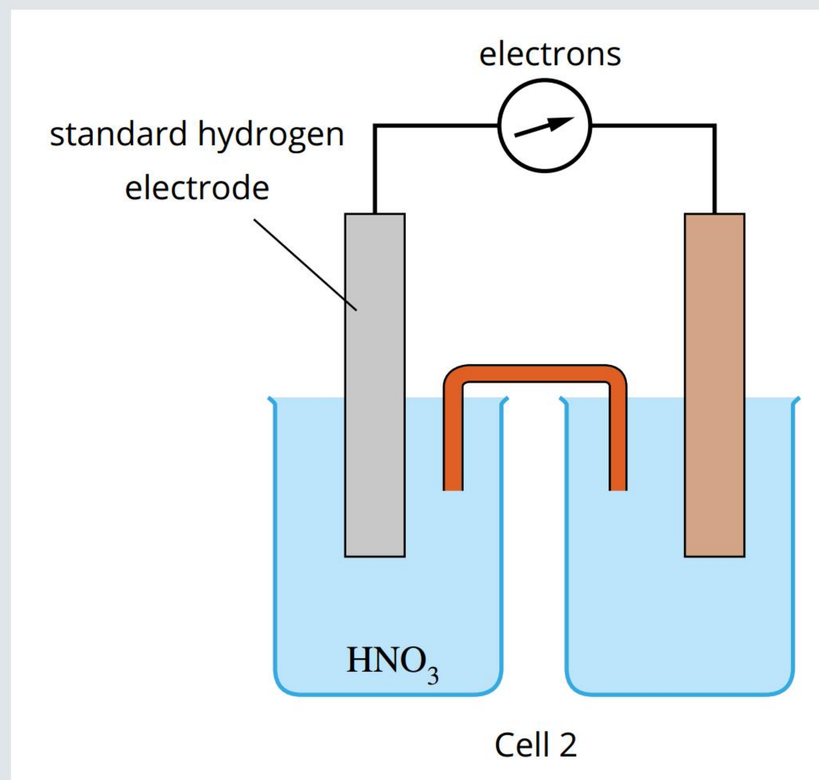
c Use the standard electrode potential values to determine the $E°$ value for the cell.

d Which of the materials listed is suitable to make the salt bridge? Justify your choice.

e If you need to make a higher voltage, describe how you could achieve this with the materials available.

37 Carefully examine the two galvanic cells set up with the standard hydrogen half-cell.





a Describe the purpose of the hydrogen half-cell.

b Suggest the composition of the electrodes and solutions of the other half-cells combined with the hydrogen half-cell in both Cell 1 and Cell 2. Justify your choice.

c Identify the polarity of the cell potentials for Cell 1 and Cell 2. That is, are they positive or negative?

Data analysis

DATA SET 1

The information below applies to Questions 1–5.

Galvanic cells (batteries in everyday language) are designed to operate at a range of temperatures; however, if the operating temperature is too extreme, the cell will not maintain its voltage. In the case of rechargeable cells, they will not recharge to their full capacity.

Lithium button batteries provide a small-size battery with a higher voltage than other alternatives.

For a particular type of cell, the oxidation reaction at the anode is provided by lithium being oxidised.

Question 1 (1 mark)

Use the table of standard electrode (reduction) potential values (Table 2 in Appendix E) to write the oxidation reaction for this cell.

The reduction reaction for this particular cell is shown below:

$$2MnO_2(s) + H_2O(l) + 2e^- \rightleftharpoons Mn_2O_3(s) + 2OH^-(aq) \quad E^o = 0.15\ V$$

Question 2 (2 marks)

Use the table of standard electrode (reduction) potential values (Table 2 in Appendix E) to write the overall reaction and the theoretical overall cell potential.

Lithium button battery

Data are collected on a group of lithium button batteries. They are operated at different temperatures and the voltage maintained is recorded every 10 hours. The data are recorded in the table below. The lithium cells chosen have a starting voltage of around 3.0 V and generally stop working when the voltage falls below 1.5 V.

The voltages of lithium batteries during discharge at different temperatures			
Time (hours)	**–15.0°C**	**0.0°C**	**25.0°C**
0.0	2.90 V	3.10 V	3.19 V
10.0	2.30 V	2.60 V	2.80 V
20.0	2.20 V	2.55 V	2.75 V
30.0	2.10 V	2.50 V	2.70 V
40.0	1.75 V	2.45 V	2.65 V
50.0	1.50 V	2.25 V	2.50 V
60.0		1.90 V	2.00 V
70.0			1.60 V

Question 3 (5 marks)

Plot a suitable graph of the data in the table to compare the voltages over time.

Question 4 (4 marks)

Describe the trend shown by the graph, and suggest an explanation for what is observed.

Question 5 (2 marks)

Examine the starting voltages for the cells and account for any variations in these voltages compared to the theoretical voltage calculated in question **2**.

CHAPTER 07

Electrolysis and electrolytic cells

A large number of chemicals are produced through electrolysis. Some of these chemicals can be difficult to obtain by other means. This makes the process of electrolysis important.

Electrolysis is used in a number of important applications in the chemical industry, such as plating a thin film of metal on the surfaces of other metals to improve their appearance or to prevent corrosion, extracting reactive metals from their ores and the production of copper and zinc.

Throughout this chapter, you will explore the reactions that occur in electrolytic cells and compare them to the reactions that occur in galvanic cells.

Syllabus subject matter

Topic 2 • Oxidation and reduction

ELECTROCHEMICAL CELLS

- Explain that electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit that allows electrons to move from the anode (oxidation reaction) to the cathode (reduction reaction). **7.1**
- Discriminate between a galvanic and an electrolytic cell. **7.1**

ELECTROLYTIC CELLS

- Identify that electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur. **7.1**
- Identify the essential components of an electrolytic cell, including the source of electric current and conductors, positive and negative electrodes and the electrolyte. **7.1**
- State the factors that affect the products in electrolysis. **7.1**
- Determine the products of the electrolysis of a molten salt. **7.1**
- Explain the products of the electrolysis of aqueous solutions, e.g. dilute and concentrated sodium chloride(aq) and copper sulfate(aq). **7.1**
- Describe that electrolytic cells can be used in small-scale and industrial situations, including metal plating and the purification of copper. **7.1**
- Calculate moles of electrons, current, time, mass of substance or volume of gas produced or used during electrolysis. (Formula: $q = n(e^-) \times F$ or $q = I \times t$) **7.2**
- Analyse data to determine the relative amounts of product produced at each electrode in electrolysis. **7.2**

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7.1 Electrolytic cells

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that an electrolytic cell uses an external energy source to force a non-spontaneous redox reaction to occur
- identify the key components of an electrolytic cell and explain how the cell operates
- construct half-equations for the processes that occur at each electrode in an electrolytic cell and use the half-equations to construct an overall equation for the cell reaction
- use standard electrode potentials to predict the reactions that will occur in different electrolytic cells
- describe some of the small-scale and industrial applications of electrolysis.

FIGURE 7.1.1 During electrolysis, electrical energy is used to make redox reactions occur. In this experiment, electricity passing through dilute sodium chloride solution creates bubbles of hydrogen gas at the left-hand electrode and bubbles of oxygen gas at the right-hand electrode. The gases are being collected in the test tubes.

In Chapter 6, you learnt that a spontaneous redox reaction can occur between an oxidising agent and a reducing agent. If the reaction occurs when the reactants are mixed directly, the chemical energy of the reactants is converted into heat energy. If, however, the same reaction occurs in a galvanic cell, the chemical reaction generates electrical energy.

In this chapter, you will learn that the reverse reaction can be made to occur in a process called electrolysis. Electrolysis involves the passage of electrical energy from a power supply, such as a battery, through a conducting liquid. The electrical energy causes non-spontaneous redox reactions to occur. An example of this is shown in Figure 7.1.1, where an electric current is being passed through a dilute sodium chloride solution, causing water to split into hydrogen gas and oxygen gas.

PRINCIPLES OF ELECTROLYSIS

Chemical reactions occur when an electric current from a direct current (DC) power supply passes through a conducting liquid. This process is called **electrolysis,** and the apparatus used for electrolysis is called an electrolytic cell. A diagram of a typical electrolytic cell is shown in Figure 7.1.2. The two electrodes in the cell act as conductors of electricity and are connected to a power supply. The electrode connected to the positive terminal of the power supply is called the positive electrode, and the electrode connected to the negative terminal is called the negative electrode.

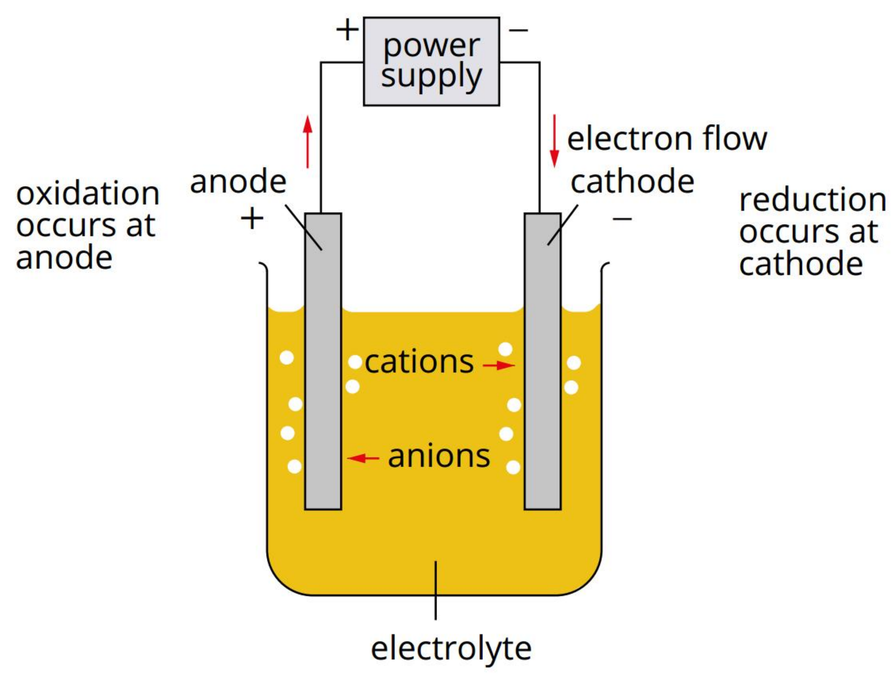


FIGURE 7.1.2 A representation of an electrolytic cell

During electrolysis, reactions occur at the surface of both electrodes. The electrical energy required for these reactions to occur is provided by the power supply. The power supply can be regarded as a type of 'electron pump', drawing electrons through the external circuit from the positive electrode and pushing them onto the negative electrode.

As a consequence, oxidation occurs at the positive electrode, which is known as the **anode**. Reduction occurs at the negative electrode, which is known as the **cathode**. This is different from the galvanic cells you were introduced to in Chapter 6, where the anode, the electrode at which oxidation occurs, is the negative electrode, and the cathode, the electrode at which reduction occurs, is the positive electrode.

The overall reaction that occurs in electrolytic cells is non-spontaneous—a reaction that would not occur naturally—and involves the conversion of electrical energy into chemical energy.

The conducting liquid in an electrolytic cell is called the **electrolyte**, and can be either a **molten** ionic salt, such as NaCl(l), or a solution of an ionic solid, such as NaCl(aq). The ions in the electrolyte move towards the electrodes to balance the charges formed during electrolysis; anions move towards the anode, and cations move towards the cathode, just as they do in galvanic cells.

The electrolytic process usually takes place in one container. Unlike galvanic cells, there is no need to locate the electrodes in separate containers because a **non-spontaneous reaction** is involved. However, the products do need to be kept apart as they are produced. Otherwise, they can spontaneously react with each other to re-form the original reactants.

Examples of electrolysis that involve molten ionic salts and solutions of ionic solids are described below.

In an electrolytic cell:

- oxidation occurs at the anode, which is the positive electrode
- reduction occurs at the cathode, which is the negative electrode.

In an electrolytic cell:

- anions move towards the anode
- cations move towards the cathode.

ELECTROLYSIS OF A MOLTEN SALT

A diagram showing the electrolysis of a molten salt, NaCl(l), in a simple electrolytic cell is shown in Figure 7.1.3.

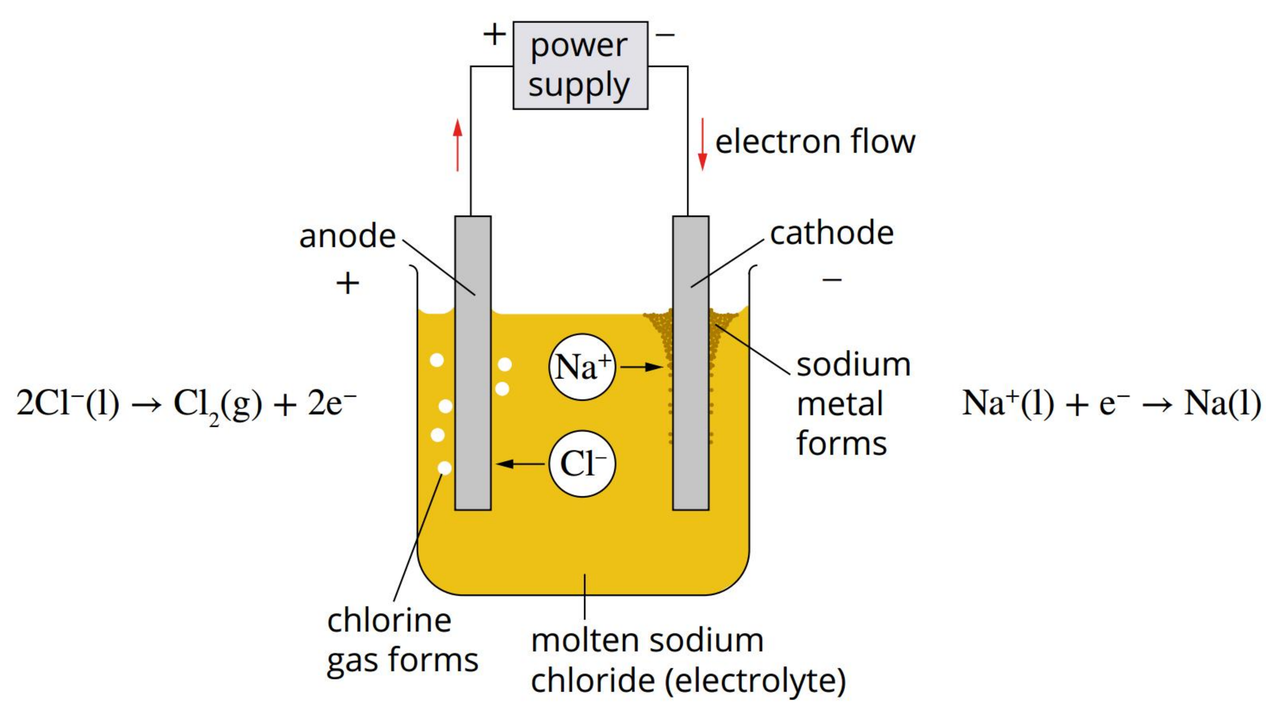


FIGURE 7.1.3 Electrolysis of molten sodium chloride, NaCl(l)

Platinum metal or graphite is used for the electrodes because they allow the passage of electrons to and from the power supply. Because platinum and graphite are **inert** (unreactive), the electrodes do not react with the contents of the cell.

The molten sodium chloride acts as an electrolyte because it is a conducting liquid. The electrolyte is composed of $Na^+(l)$ ions and $Cl^-(l)$ ions. Sodium chloride melts at 801°C, so this process must occur at a high temperature. No water is present.

At the negative electrode

The power supply pushes electrons towards the negative electrode. $Na^+(l)$ ions in the electrolyte are attracted to the negative electrode, where they accept electrons and become sodium atoms:

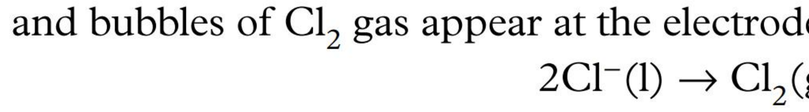
$$Na^+(l) + e^- \rightarrow Na(l)$$

Because this is a reduction reaction, this electrode is known as the cathode.

Sodium is solid at room temperature, but it is liquid at the temperatures required to melt sodium chloride. It is less dense than molten sodium chloride and floats to the top of the cell.

At the positive electrode

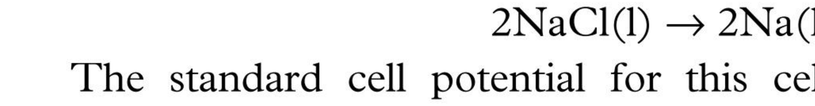
Chloride ions in the electrolyte migrate towards the positive electrode to give up electrons, forming chlorine atoms. These atoms quickly form chlorine molecules and bubbles of Cl_2 gas appear at the electrode:



$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

The electrons from the chloride ions move through the electrode towards the power supply. Because this is an oxidation reaction, this electrode is known as the anode.

The overall reaction that takes place in the cell is:



$$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$$

The standard cell potential for this cell is –4.07 V, which means it is a non-spontaneous reaction. The electrical energy from the power supply is converted into chemical energy in the products.

Since Cl_2 is a strong oxidising agent and Na is a strong reducing agent, the products at the two electrodes must be kept apart. Otherwise, they will spontaneously react to re-form sodium chloride.

The Downs cell

The electrolysis of molten sodium chloride described above is performed on a commercial scale to produce sodium and chlorine. The electrolytic cell used for this purpose is called the Downs cell, as shown in Figure 7.1.4.

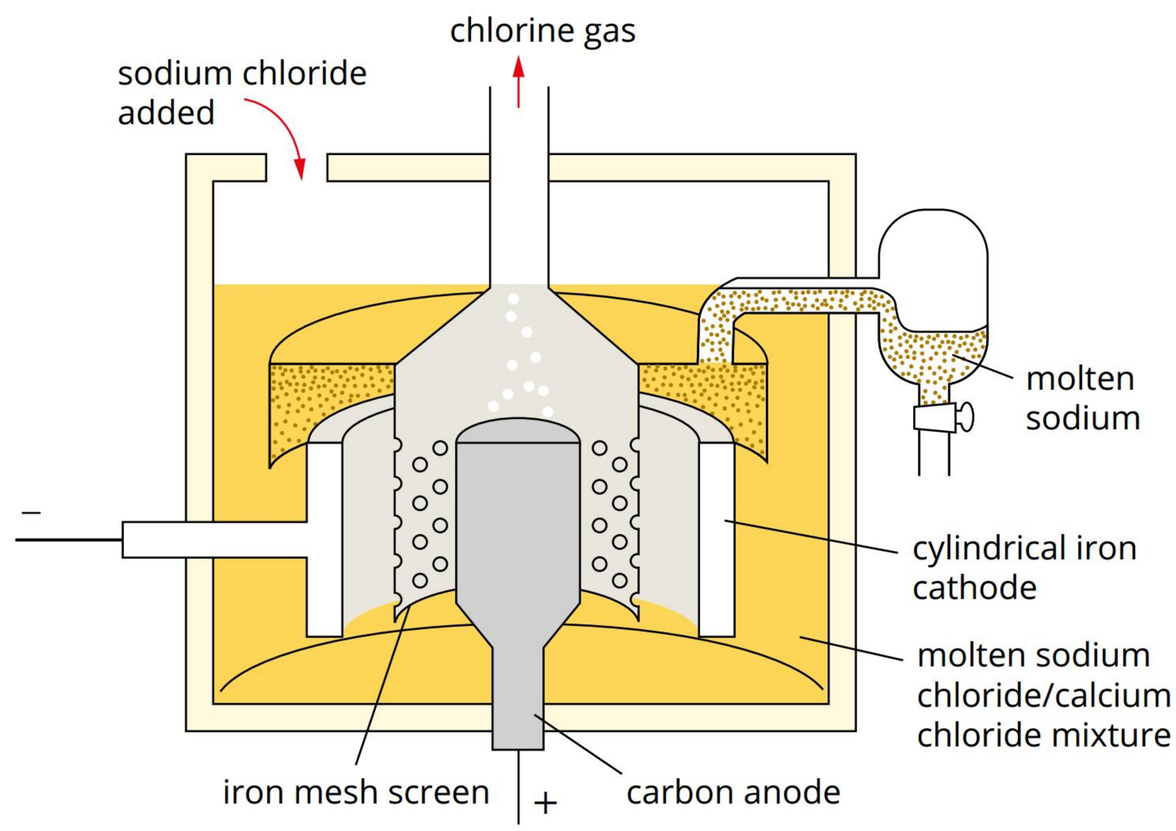


FIGURE 7.1.4 A diagram of a Downs cell, which produces chlorine gas and sodium

The anode of the Downs cell is made of an inert conducting material, such as graphite or platinum, and is not consumed in the reaction. The cathode is made of iron, which is effectively inert because electrons are pumped onto this electrode, preventing the iron from reacting.

In the electrolysis of a molten electrolyte:

- anions are oxidised at the anode (positive)
- cations are reduced at the cathode (negative)
- water is not present because it would interfere with the desired reactions.

An iron mesh screen is used in the cell to keep the products at the anode and cathode apart, preventing the Cl_2 and Na formed from reacting and re-forming sodium chloride.

The advantage of using a molten electrolyte in the Downs cell is that there is no water present to interfere with the desired reactions. As you will learn later, if aqueous sodium chloride were used as the electrolyte instead of molten sodium chloride, water would react at the cathode and form hydrogen gas.

In general, the main disadvantage of using a molten electrolyte is that the process requires much more energy. Energy must be expended to maintain the electrolyte in a molten state and at the temperature needed for electrolysis to proceed efficiently.

ELECTROLYSIS OF AQUEOUS SOLUTIONS

In some electrolytic cells, there may be several chemicals present at each electrode that might be able to react. If an aqueous electrolyte is used instead of a molten salt, then water is a potential reactant. Even the material used for the electrodes may participate in the reaction.

In these cases, you can use the table of standard electrode (reduction) potentials (Table 2 in Appendix E) to predict which of the possible reactions would be most likely to occur.

During electrolysis, the:

- strongest oxidising agent usually reacts at the cathode
- strongest reducing agent usually reacts at the anode.

To illustrate this, we will examine the electrolysis of an aqueous solution of sodium chloride.

> Just as in galvanic cells, in electrolytic cells, the strongest reducing agent reacts at the anode and the strongest oxidising agent reacts at the cathode.

Electrolysis of sodium chloride solution

Consider the electrolysis of a 1.0 mol L^{-1} solution of sodium chloride using **inert electrodes**, as shown in Figure 7.1.5. With water present in the cell as well as $Na^+(aq)$ and $Cl^-(aq)$, there are a number of species that might be able to react.

- $H_2O(l)$ could be both oxidised and reduced.
- $Na^+(aq)$ ions could be reduced.
- $Cl^-(aq)$ ions could be oxidised.

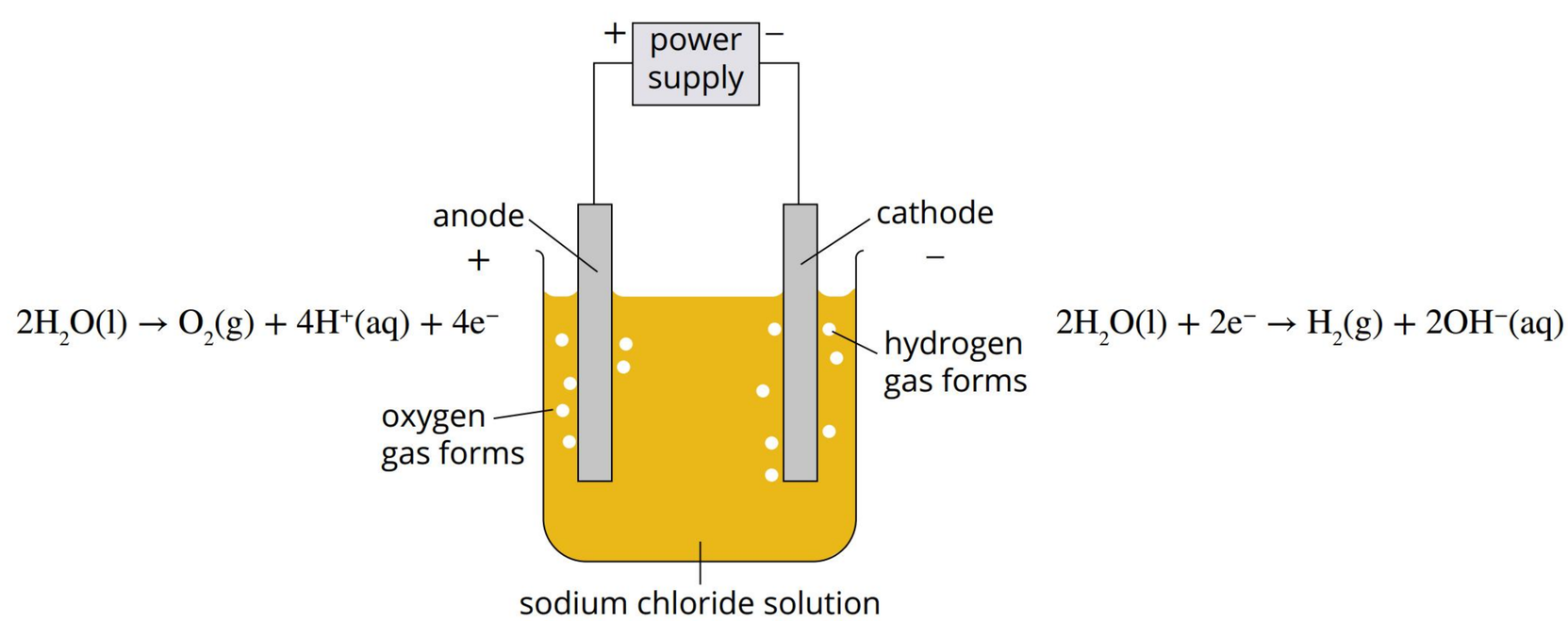


FIGURE 7.1.5 Electrolysis of aqueous sodium chloride solution

In Chapter 6, you learnt that the **standard electrode (reduction) potentials** can be used to predict the reactions that will occur in a galvanic cell. They can be used in a similar way to predict the likely reactions that will occur in an electrolytic cell.

The relevant half-equations for the species present in an aqueous solution of NaCl are listed in the following list in the order of increasing reduction potentials. The species present are highlighted in bold print.

$$\mathbf{Na^+(aq)} + e^- \rightleftharpoons Na(s) \qquad E^\circ = -2.71\,V$$
$$\mathbf{2H_2O(l)} + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \qquad E^\circ = -0.83\,V$$
$$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons \mathbf{2H_2O(l)} \qquad E^\circ = 1.23\,V$$
$$Cl_2(g) + 2e^- \rightleftharpoons \mathbf{2Cl^-(aq)} \qquad E^\circ = 1.36\,V$$

Inspection of these half-equations shows that there:

- are two possible reduction reactions
- are two possible oxidation reactions
- is no combination of reactants that will react spontaneously; therefore, an external power supply is required.

At the cathode

The power supply pushes electrons towards the negative electrode, and $Na^+(aq)$ ions are attracted to the negative electrode. If you look on the left-hand side of the table of standard electrode potentials (Table 6.2.1 on page 195 in Chapter 6 and Table 2 in Appendix E), you will see that there are two species in the cell that can act as oxidising agents, and therefore could be reduced at this electrode. These two species are $H_2O(l)$ and $Na^+(aq)$:

$$Na^+(aq) + e^- \rightarrow Na(s) \qquad E^\circ = -2.71\,V$$
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ = -0.83\,V$$

Reactions lower in Table 6.2.1 involve stronger oxidising agents and are more likely to occur as reduction reactions. The reduction of water requires less energy than the reduction of sodium ions (the E° of the half-equation for $H_2O(l)$ is less negative than the E° of the half-equation for $Na^+(aq)$). Therefore, water will be reduced at the cathode to form hydrogen gas.

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

The sodium ions will not react and will remain in solution as spectator ions.

At the anode

Electrons are withdrawn from this electrode by the power supply. There are two species in the cell, $Cl^-(aq)$ and $H_2O(l)$, that are on the right-hand side of Table 6.2.1 and can act as reducing agents and could be oxidised at this electrode:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E^\circ = -1.23\,V$$
$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad E^\circ = -1.36\,V$$

Reactions higher in the table involve stronger reducing agents and have a greater tendency to occur as oxidation reactions. While the two reactions are close together in the series, the oxidation of water requires less energy than the oxidation of chloride ions (water reacts in preference to Cl^- ions because it is positioned higher on Table 6.2.1). The predicted anode reaction is:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

The overall reaction can be written as the sum of the reduction and oxidation half-equations:

$$(2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)) \times 2 \qquad \text{(reduction)}$$
$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad \text{(oxidation)}$$

$$6H_2O(l) \rightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$$

When the $H^+(aq)$ ions formed at the anode come in contact with the $OH^-(aq)$ ions formed at the cathode, they react to form water. Thus, the overall equation can be written as:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

Therefore, water is split into its elements in this process.

Electrolysis of concentrated sodium chloride solution

In practice, it is possible for either of the anode reactions to occur when sodium chloride solution is electrolysed, depending on conditions such as the concentration of the solution. In some cases, $O_2(g)$ and $H^+(aq)$ are formed, and in others, $Cl_2(g)$ is produced.

Recall that the standard electrode potentials shown in Table 6.2.1 were determined for reactions under standard conditions (concentrations of 1 mol L^{-1}, gas pressures of 100 kPa) and at a temperature of 273 K. When the conditions are not standard and the concentration of sodium chloride is much higher than 1 mol L^{-1}, chlorine gas is produced at the anode.

Comparing molten and aqueous electrolytes

Table 7.1.1 summarises the differences between the reactions that occur during the electrolysis of molten and aqueous sodium chloride. Note that the products formed at each electrode depend on the state and, in the case of an aqueous electrolyte, on the concentration of the electrolyte.

TABLE 7.1.1 A comparison of the electrolysis of molten NaCl with aqueous NaCl

	Molten NaCl	Aqueous dilute NaCl	Aqueous concentrated NaCl
Temperature	high	room temperature	room temperature
Anode reaction	$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
Cathode reaction	$Na^+(l) + e^- \rightarrow Na(l)$	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
Overall reaction	$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$	$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$	$2Cl^-(l) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)$

Where possible, aqueous electrolytes are used in industrial situations in preference to molten electrolytes. It takes energy to maintain an electrolyte in a molten state and so a cell that uses an aqueous electrolyte is usually more cost-effective.

The products formed at the electrodes in an electrolytic cell depend on the state and, in the case of an aqueous electrolyte, the concentration of the electrolyte.

ELECTROLYSIS INVOLVING REACTIVE ELECTRODES

In the examples of electrolysis that you have encountered so far, the electrodes do not take part in the reaction and are described as inert electrodes. However, in many electrolytic cells, the electrodes are consumed in the cell reaction. Such electrodes are called **reactive electrodes**.

Consider the electrolysis of a 1.0 mol L^{-1} solution of copper(II) sulfate using copper electrodes, as shown in Figure 7.1.6. With water present in the cell, as well as $Cu^{2+}(aq)$ and the copper electrodes, the following species might react (Note that $SO_4^{2-}(aq)$ ions do not react under these conditions):

- $H_2O(l)$ could be oxidised at the anode and reduced at the cathode.
- $Cu^{2+}(aq)$ ions could be reduced at the cathode.
- $Cu(s)$ metal in the electrodes could be oxidised at the the anode.

The possible reactions that could occur at each electrode are considered in detail now.

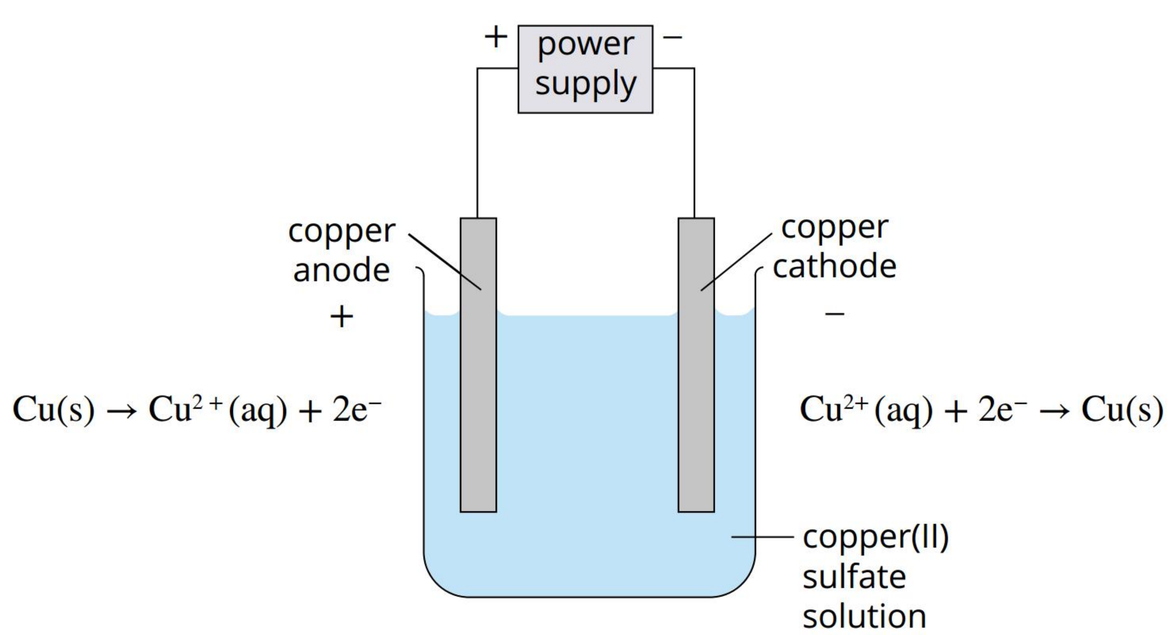


FIGURE 7.1.6 Electrolysis of copper(II) sulfate solution

At the cathode

If you look on the left-hand side of Table 6.2.1, you will see that the species in the cell that can act as oxidising agents are $Cu^{2+}(aq)$ and $H_2O(l)$:

$$\mathbf{Cu^{2+}(aq)} + 2e^- \rightleftharpoons Cu(s) \qquad E^\circ = +0.34\,V$$

$$\mathbf{2H_2O(l)} + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \qquad E^\circ = -0.83\,V$$

Reactions lower in Table 6.2.1 (with more positive E° values) involve stronger oxidising agents and are more likely to occur as reduction reactions. Therefore, $Cu^{2+}(aq)$ ions will be reduced at the cathode, and a layer of copper metal will be deposited:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

At the anode

On the right-hand side of Table 6.2.1 are species in the cell that can act as reducing agents and could be oxidised at the anode. In this example, they include the copper electrode and $H_2O(l)$:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons \mathbf{Cu(s)} \qquad E^\circ = +0.34\,V$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons \mathbf{2H_2O(l)} \qquad E^\circ = +1.23\,V$$

Reactions higher in Table 6.2.1 (with a more negative E° value) involve stronger reducing agents and have a greater tendency to occur as oxidation reactions. The predicted oxidation reaction that occurs at the anode is therefore:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

The metal anode will dissolve to form $Cu^{2+}(aq)$ ions.

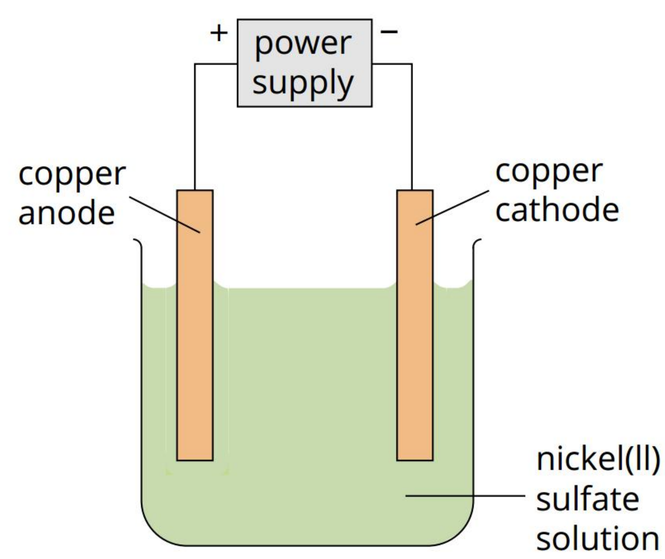
Note that, for this particular cell, when you add the anode and cathode half-reactions together, all species cancel and there is no overall reaction. The overall concentration of $Cu^{2+}(aq)$ ions in the electrolyte remains constant. However, copper metal at the anode will dissolve, and copper metal will be formed at the cathode. The metal is being transferred from one electrode to the other by electrical energy.

This process is used as the basis of a technique for purifying copper metal, called **electrorefining**, which is described later in this module.

Worked example 7.1.1

PREDICTING THE PRODUCTS OF ELECTROLYSIS

Use the table of standard electrode potentials (Table 6.2.1 or Table 2 in Appendix E) to predict the products of the electrolysis of 1 mol L^{-1} nickel(II) sulfate solution with copper electrodes at 25°C. A diagram of this electrolytic process is shown below.



Thinking	Working
Identify which species are present in the solution.	$Ni^{2+}(aq)$, $SO_4^{2-}(aq)$ and $H_2O(l)$
Identify what the electrodes are made of.	copper (Cu(s))
Refer to the table of standard electrode potentials (Table 6.2.1 or Table 2 in Appendix E) to identify the possible reactions. Write these half-equations in the order they appear in the table.	By referring to the table of standard electrode potentials, you can see that a number of reactions need to be considered because the cell contains two oxidising agents, $Ni^{2+}(aq)$ and $H_2O(l)$ (which could be reduced at the cathode), and two reducing agents, Cu(s) and $H_2O(l)$ (which could be oxidised at the anode). $\mathbf{2H_2O(l)} + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E° = -0.83$ V $\mathbf{Ni^{2+}(aq)} + 2e^- \rightleftharpoons Ni(s)$ $E° = -0.24$ V $Cu^{2+}(aq) + 2e^- \rightleftharpoons \mathbf{Cu(s)}$ $E° = +0.34$ V $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons \mathbf{2H_2O(l)}$ $E° = +1.23$ V The $SO_4^{2-}(aq)$ ions are not involved in the reaction.
Determine the reactions that could occur at the anode.	At the anode (+), oxidation reactions that could occur are: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Determine the most likely reaction at the anode.	Reactions higher in Table 6.2.1 (with a more negative $E°$ value) involve stronger reducing agents and have a greater tendency to occur as oxidation reactions. The strongest reducing agent (half-equation with the more negative $E°$ value), Cu(s), will therefore be oxidised at the anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Determine the reactions that could occur at the cathode.	At the cathode (−), reduction reactions that could occur are: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
Determine the most likely reaction at the cathode.	Reactions lower in Table 6.2.1 (with more positive $E°$ values) involve stronger oxidising agents and are more likely to occur as reduction reactions. The strongest oxidising agent (half-equation with the more positive $E°$ value), $Ni^{2+}(aq)$, will therefore be reduced at the cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
Combine the two half-reactions to obtain the overall reaction in the electrolytic cell.	The overall redox reaction can be represented by the following equation: $Ni^{2+}(aq) + Cu(s) \rightarrow Ni(s) + Cu^{2+}(aq)$ The overall $E°_{cell}$ value for the cell is given by: $E°_{cell} = E°_{reduction} - E°_{oxidation}$ $E°_{cell} = E°_{Ni^{2+}/Ni} - E°_{Cu^{2+}/Cu}$ $E°_{cell} = -0.24 - 0.34 = -0.58\,V$ The negative value for $E°_{cell}$ indicates that the redox reaction is not spontaneous and requires electrical energy to produce the chemical change (i.e. electrolysis)

➤ Try yourself 7.1.1

PREDICTING THE PRODUCTS OF ELECTROLYSIS

Use the table of standard electrode potentials (Table 2 in Appendix E) to predict the products of electrolysis of 1 mol L^{-1} zinc sulfate solution with copper electrodes at 25°C.

It is important to bear in mind that, while the table of standard reduction potentials can be used in this way to make predictions, the series is based on standard conditions. Most of the electrolysis reactions that occur in the laboratory and in industry are not under standard conditions. Experiments are the only sure way to find out what products form in a particular instance. In practice, reactions are affected by factors such as electrolyte concentration, gas pressures, current, voltage and the use of different electrodes.

APPLICATIONS OF ELECTROLYSIS

Chemical industries tend to avoid using electrolysis for the manufacture of chemicals because of the relatively high cost of electrical energy. Nevertheless, this process enables some chemicals to be produced that could not be readily produced any other way.

Earlier, you saw that sodium and chlorine are manufactured commercially by electrolysis using the Downs cell. Let us now look at two further industrial applications of electrolysis: **electroplating** and electrorefining.

Electroplating

If you browse through a jewellery store, you will see many shiny 'silver' articles, such as bracelets, necklaces and trays. The main materials present in many of these articles will be inexpensive metals such as copper, zinc and nickel—not silver! Often, the only silver present is a thin surface coating only a fraction of a millimetre thick that has been applied by electrolysis.

The deposition of a layer of metal on the surface of another metal is called electroplating. Electroplating plants can be found in both small-scale and large-scale industry operations. (Figure 7.1.7).

FIGURE 7.1.7 A worker prepares a rack of objects for immersion in an electroplating tank. The objects to be plated are connected to the negative electrode. The positive electrode is usually made of the metal that is being coated.

While electroplating can be used to make an object more decorative, it can also be used to improve the resistance of metals to corrosion. For example, 'tin' cans are used extensively for packaging food items such as soups, fruit and fish, as shown in Figure 7.1.8. Although they are commonly called 'tin' cans, they are mainly composed of steel, which is an alloy of iron and carbon. There is just a thin layer of tin plated over the surface of the steel can. Tin corrodes very slowly and prevents contact between the iron, moisture and air. Effectively, the tin prevents the iron from rusting.

FIGURE 7.1.8 Tin cans are used as packaging for a wide range of products. The tin coating on the can prevents it from corroding.

Electroplating is performed in electrolytic cells, like the simplified one shown in Figure 7.1.9 for tin plating. The object to be plated is connected by a wire to the negative terminal of a power supply. This object becomes the negative electrode in the cell.

The object is immersed in an electrolyte, such as tin(II) nitrate solution, which contains ions of the metal to be plated. The $Sn^{2+}(aq)$ ions in the solution move towards the negative electrode (the object to be plated) and are reduced. The $NO_3^-(aq)$ ions move towards the positive electrode, allowing current to pass through the cell.

An electrode of tin metal is connected to the positive terminal of the power supply.

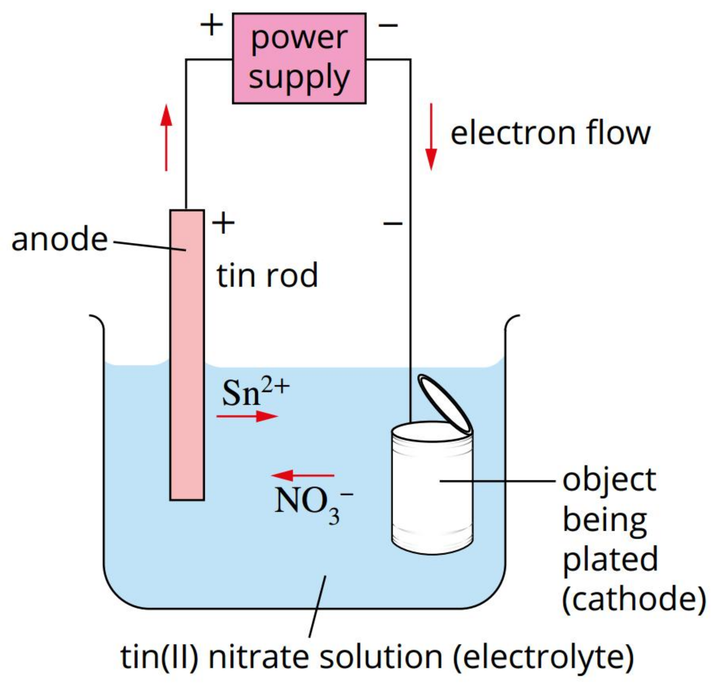


FIGURE 7.1.9 A cell used for electroplating tin

At the negative electrode (cathode)

As shown in Figure 7.1.10, Sn^{2+} ions are attracted to the negative electrode, where they accept electrons and are reduced to tin metal:

$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$$

A coating of tin is formed on the object.

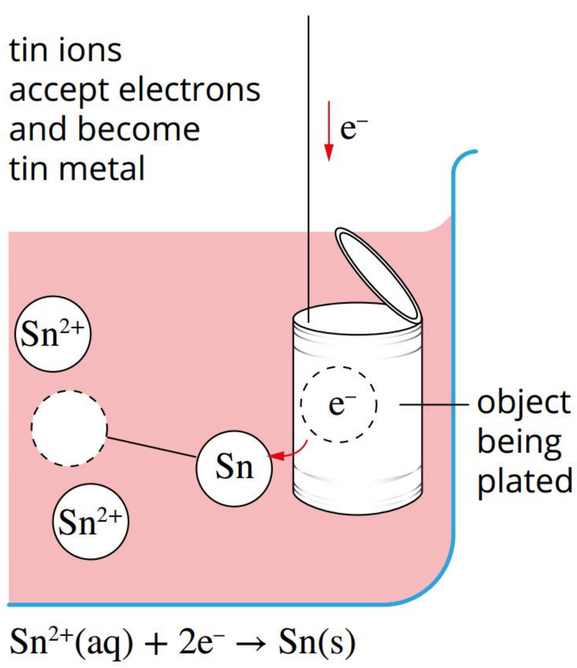


FIGURE 7.1.10 A representation of the reaction at the cathode in the process of tin plating

> **The set-up of an electroplating cell can be summarised as follows.**
>
> - **The object being plated is at the cathode (negative).**
> - **An electrode of the metal to be plated is used as the anode (positive).**

At the positive electrode (anode)

As shown in Figure 7.1.11, the positive terminal of the power supply draws electrons from the tin electrode, causing an oxidation reaction to occur. Tin metal slowly dissolves as $Sn^{2+}(aq)$ ions are formed:

$$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$$

This reaction replaces $Sn^{2+}(aq)$ ions in solution that were consumed by the reaction at the negative electrode. The concentration of tin ions in the electrolyte therefore remains constant.

Although the $NO_3^-(aq)$ ions in the electrolyte are attracted to the anode, they cannot be oxidised because nitrogen is already in its highest oxidation state (+5). As a result, the $NO_3^-(aq)$ ions are not involved in the electrode reactions of the cell.

The overall result of the electroplating process is that the metal anode dissolves, and a coating of metal is formed on the object at the cathode.

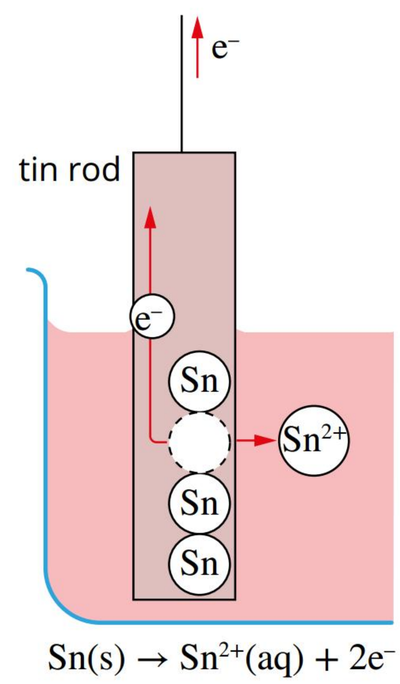


FIGURE 7.1.11 A representation of the reaction at the anode in the process of tin plating

Electrorefining of copper

Copper metal is extracted from its ores by **smelting**. The process involves several stages, finishing with the copper ore being heated strongly in air to produce impure copper metal.

As hot gases escape, the copper surface becomes blistered, and it is commonly known as 'blister copper'. It contains about 2% of impurities such as sulfur, iron, antimony, silver and gold.

Blister copper is purified by electrolysis. Sheets of blister copper are placed in a large tank of sulfuric acid, and thin sheets of pure copper are positioned between them. An external power source is connected so that the blister copper acts as a positive electrode (anode) and the pure copper acts as a negative electrode (cathode), as shown in Figure 7.1.12.

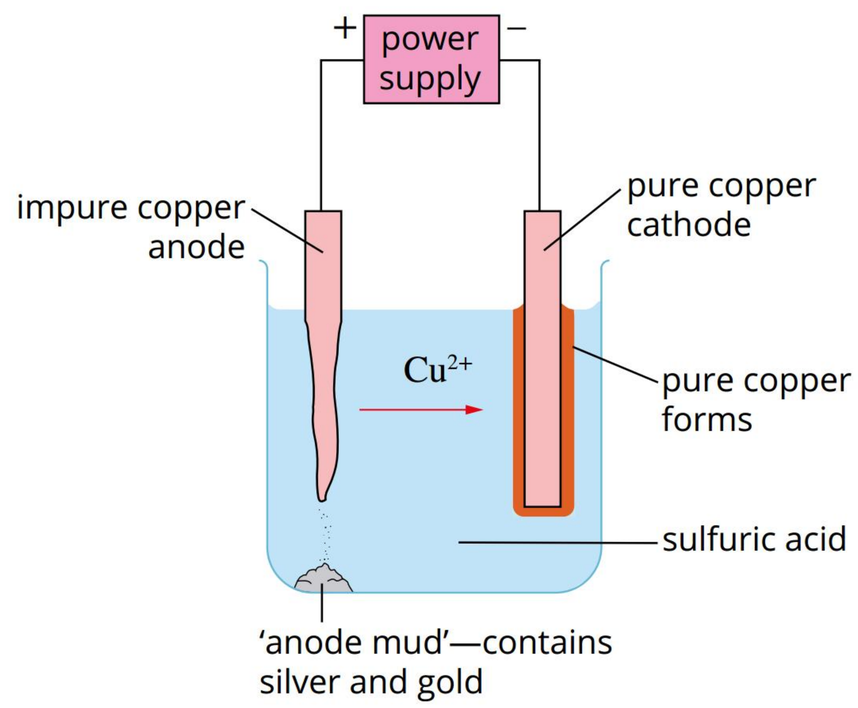


FIGURE 7.1.12 Electrorefining of copper metal by electrolysis

At the anode, electrons are drawn away from the blister copper to the positive terminal of the power source. Copper and impurities more reactive than copper, such as nickel and zinc, are oxidised and enter the solution as ions:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

Impurities less reactive than copper, such as silver, gold and platinum, are not oxidised and simply fall from the anode, collecting at the bottom of the tank. This anode residue is sometimes called 'anode mud'. The precious metals are later recovered from the valuable mud.

At the pure copper cathode, copper metal is deposited as electrons from the power source are accepted by metal ions from solution. Since copper ions are the strongest oxidising agents present in solution, copper is the only metal formed:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Copper of 99.99% purity is obtained this way.

Electrorefining uses a lot of electrical energy, so a refinery must be located close to a source of abundant, cheap power. Because of this, copper produced in the smelter at Mount Isa in Queensland is shipped to Townsville for refining. Australia ranks eighth in the world in terms of copper production.

COMPARISON OF ELECTROLYTIC AND GALVANIC CELLS

Before concluding this module, let us compare the features of electrolytic cells with those of galvanic cells that you studied in Chapter 6. Galvanic and electrolytic cells are both types of electrochemical cells. While both cells involve the conversion between electrical energy and chemical energy, there are important differences between them.

Table 7.1.2 and Figure 7.1.13 summarise the similarities and differences between galvanic and electrolytic cells.

TABLE 7.1.2 A summary of the similarities and differences between galvanic and electrolytic cells

Galvanic cells	Electrolytic cells
produce electricity	consume electricity
involve spontaneous reactions	involve non-spontaneous reactions
convert chemical energy into electrical energy	convert electrical energy into chemical energy
oxidation occurs at the anode	oxidation occurs at the anode
reduction occurs at the cathode	reduction occurs at the cathode
anode is negative	anode is positive
cathode is positive	cathode is negative

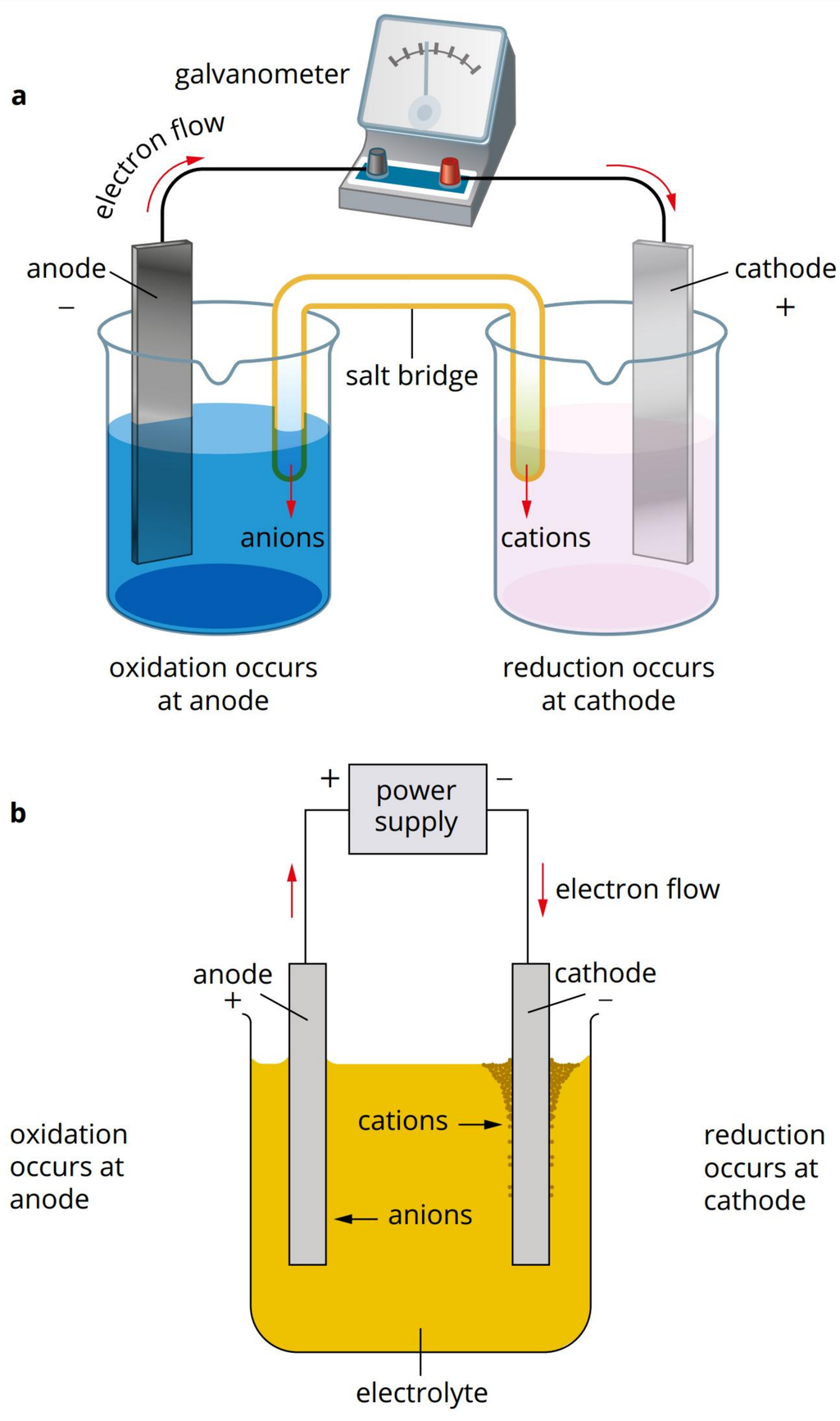


FIGURE 7.1.13 General construction of (a) a galvanic cell and (b) an electrolytic cell

7.1 Review

SUMMARY

- Electrolytic cells convert electrical energy into chemical energy, whereas galvanic cells convert chemical energy into electrical energy.
- Non-spontaneous redox reactions occur in electrolytic cells.
- The anode is defined as the electrode at which oxidation occurs; the cathode is the electrode at which reduction occurs.
- In electrolytic cells, the anode is the positive electrode and the cathode is the negative electrode.
- When several reactions may be possible at the anode of a particular cell, generally, the strongest reducing agent undergoes oxidation. Reactions with more negative E° values involve stronger reducing agents and are more likely to occur as oxidation reactions.
- When several reactions may be possible at the cathode of a particular cell, generally, the strongest oxidising agent undergoes reduction. Reactions with more positive E° values involve stronger oxidising agents and are more likely to occur as reduction reactions.
- The table of standard electrode potentials (Table 2 in Appendix E) can be used to predict the products of electrolysis.
- The electrodes used in electrolysis can be either inert or reactive.
- Both molten and aqueous electrolytes can be used in electrolysis.
- Electrolysis has a wide range of uses, including electroplating, electrorefining and water purification. Commercial applications of electrolysis are found in small-scale and industrial situations.

KEY QUESTIONS

Describe

1 Recall the meaning of the following terms.

a anode
b electrolyte
c inert electrode
d electrolytic cell
e electrochemical cell

2 Select the correct words, in bold print, to complete the following statements.
In electrolytic cells:

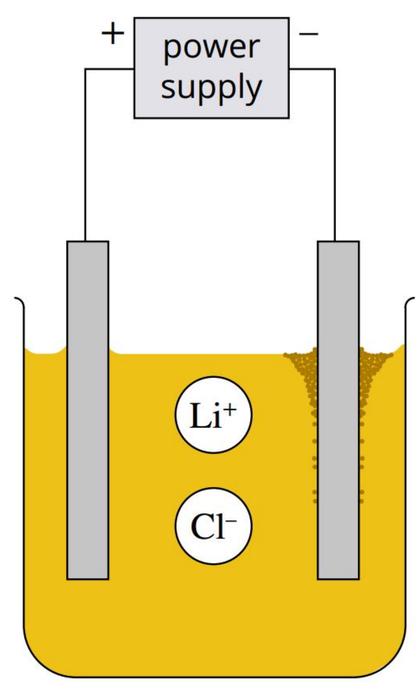
a the reactions are **spontaneous/non-spontaneous**
b **chemical/electrical** energy is converted into **chemical/electrical** energy
c the anode is **negative/positive**, and the cathode is **negative/positive**
d **oxidation/reduction** occurs at the anode, and **oxidation/reduction** occurs at the cathode
e if several reactions are possible at the anode, the strongest **oxidising/reducing** agent usually undergoes oxidation.

3 List three industrial uses for electrolysis.

Apply

4 The following diagram shows an electrolytic cell that uses molten lithium chloride (LiCl) as the electrolyte.

a Identify the anode, cathode, positive electrode and negative electrode.
b Use arrows to show the direction of electron flow and movement of the $Li^+(l)$ and $Cl^-(l)$ ions in the cell.
c Write half-equations for the reactions that occur at the:
i anode
ii cathode.



5 **a** Draw a diagram of a cell suitable for copper plating a key that uses a rod of copper metal as the anode, labelling the positive and negative electrodes.
b Determine a suitable electrolyte for the cell.
c Explain what happens to the concentration of metal ions in the electrolyte as the cell is in use.

6 Determine whether the following statements about a copper electrorefining cell are true or false.

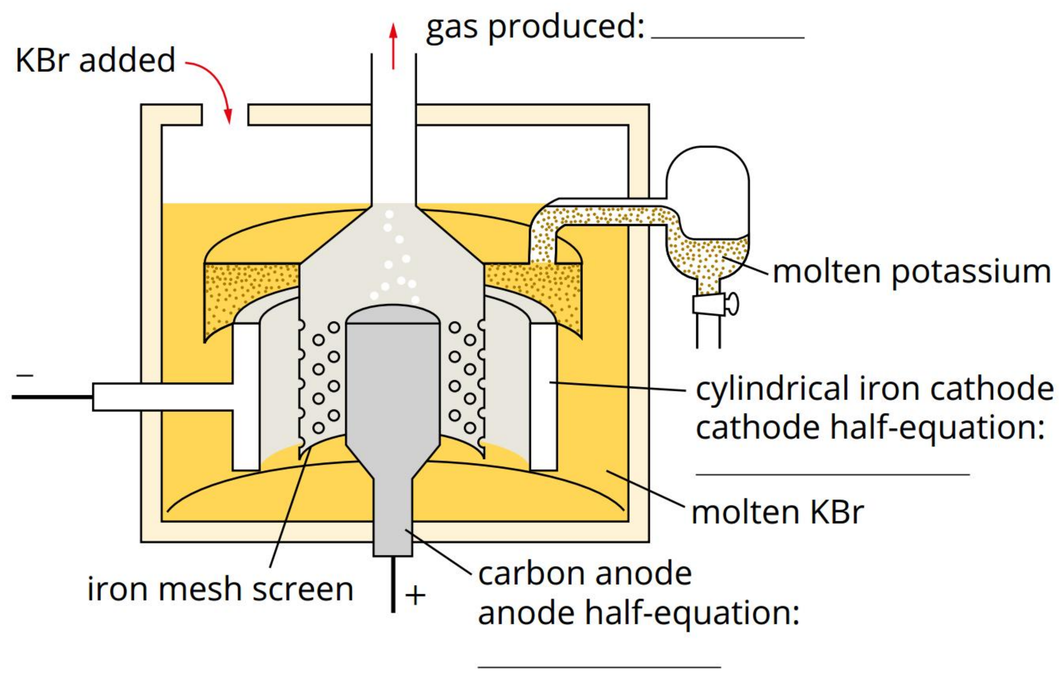
a Impure copper is the anode of the cell.

b The electrolyte in the cell is molten copper chloride.

c Pure copper is collected at the positive electrode.

d The concentration of $Cu^{2+}(aq)$ ions in the electrolyte remains constant during the electrorefining process.

7 In the cell shown in the diagram, potassium can be produced by using molten potassium bromide as the electrolyte. Complete the missing labels for this cell.



8 In an electrolysis experiment, a student is provided with an aqueous solution of nickel(II) nitrate ($Ni(NO_3)_2$). The student sets up an electrolytic cell using an unreactive carbon rod as the positive electrode and a nickel rod as the negative electrode.

a Determine on which electrode a nickel coating will appear during the operation of the cell.

b Write the half-equations for the reactions that occur at each electrode.

c Write an equation for the overall reaction.

Analyse

9 A student sets up an electrolysis experiment using a cell made of a lead anode, an iron cathode and a magnesium nitrate solution as the electrolyte.

a Refer to the table of standard electrode potentials (Table 2 in Appendix E) and identify the possible reactions that could occur. Write these half-equations in the order they appear in the series.

b Write the equations for the reactions that occur at the anode and cathode.

c Write an equation for the overall reaction.

10 An electrolytic cell was constructed using a copper electrode and an iron electrode in a zinc nitrate solution. The copper electrode was connected to the positive terminal of the power supply, and the iron electrode was connected to the negative terminal.

a Write the half-equations for the reactions that occur at the anode and cathode.

b Write an equation for the overall reaction.

11 Using the table of standard electrode potentials (Table 2 in Appendix E), determine the products at each electrode for the electrolysis of:

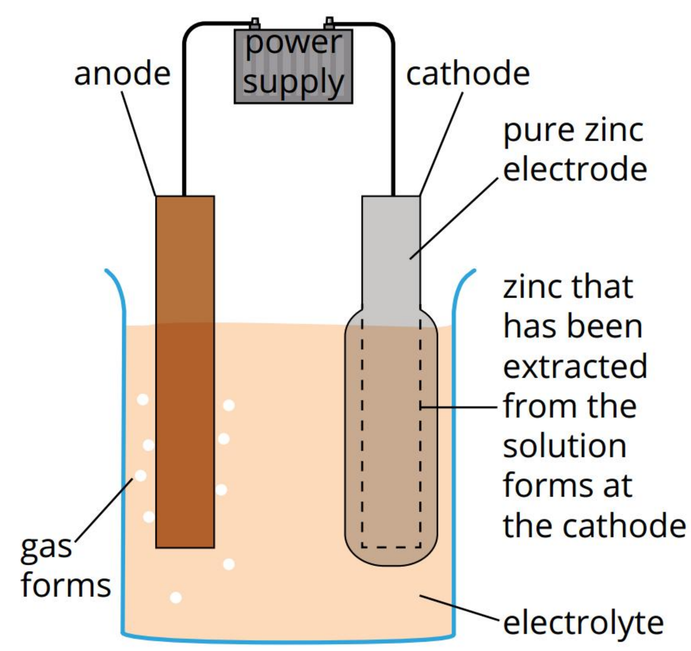
a molten calcium iodide using platinum electrodes

b molten sodium bromide using graphite electrodes

c a 1.0 mol L^{-1} aqueous solution of calcium iodide using platinum electrodes

d a 1.0 mol L^{-1} aqueous solution of sodium bromide using copper electrodes.

12 Zinc can be extracted from its compounds by electrolysis at room temperature with the cell shown in the diagram.



a Explain why an aqueous solution of zinc nitrate, instead of molten zinc nitrate, is used as the electrolyte in this cell.

b Determine the gas formed at the anode.

13 Explain why:

a most chlorine is produced by electrolysis of sodium chloride solution, rather than by the electrolysis of the molten salt

b fluorine was first isolated from fluorine compounds by electrolysis

c although zinc is an impurity in blister copper, zinc metal is not formed at the cathode in an electrorefining cell (see Figure 7.1.12 on page 224).

Continued over page

7.1 Review *continued*

14 Use the table of standard electrode potentials (Table 2 in Appendix E) to determine why aluminium cannot be produced by the electrolysis of aqueous solutions of aluminium compounds.

15 Compare an electrolytic cell with a galvanic cell. Describe two ways in which the cells are:

a different

b similar.

16 Describe two factors that affect the products in electrolysis.

17 Explain, using half-equations, what would be observed at each electrode when a solution of $CuSO_4$ undergoes electrolysis using platinum electrodes. In your response, describe what you would see in the solution around the anode.

18 Explain, using half-cell equations, what would be observed when a dilute HCl solution is electrolysed using a copper anode and an inert cathode.

19 Explain why sodium metal cannot be produced by electrolysis of aqueous NaCl.

20 Determine the minimum voltage required to electrolyse a dilute solution of LiI.

21 **a** Determine the products of the electrolysis of molten aluminium oxide (Al_2O_3).

b Describe what would be observed at each electrode and determine the direction of the electron flow in the external circuit.

7.2 Coulometric analysis

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- use Faraday's first law of electrolysis to calculate the number of moles of electrons, current and time involved in electrolysis
- apply Faraday's laws of electrolysis to determine the mass of substance or volume of gas produced or used during electrolysis
- analyse data to determine the relative amounts of product produced at each electrode in electrolysis.

In 1834, English scientist Michael Faraday published a groundbreaking series of papers detailing metal deposition experiments using electrolysis cells like those described in Module 7.1. His experiments revealed, for the first time, a quantitative relationship between the amount of electric charge passed during electrolysis and the mass of metal deposited or gas evolved at the electrodes. From these findings, Faraday formulated his two laws of electrolysis, which became fundamental principles in electrochemistry.

The process of quantifying the total charge passed in an electrochemical reaction became known as coulometry, and its application in chemical analysis is called coulometric analysis. These techniques, grounded in Faraday's laws, are now widely used in analytical chemistry to accurately determine the amount or concentration of substances based on the measurement electric charge.

In this module, you will explore Faraday's laws of electrolysis and learn how to perform calculations using the principles of coulometric analysis.

FARADAY'S LAWS OF ELECTROLYSIS

Several key factors determine the amounts of products that will form at electrodes in an electrolytic cell, including the:

- charge on the ion involved in the electrode reaction
- current flowing through the cell
- length of time that the current flows.

Faraday described the relationships between these factors. You will now apply your knowledge of electrolysis to learn about Faraday's laws and coulometric analysis.

FARADAY'S FIRST LAW OF ELECTROLYSIS

An electroplating cell can be constructed as shown in Figure 7.2.1. The variable resistor shown is used to keep the electrical current constant.

This cell can be used to study the relationship between the mass of metal deposited at the cathode and the quantity of charge that passes through the cell. Although the mass of metal formed is easily measured by weighing the cathode, the electric charge is determined indirectly.

Electric charge, symbol Q, is measured using the unit **coulombs** (C). The electric charge passing through a cell may be calculated from measurements of the current, I, through the cell and the time, t, for which the current flows. Current is measured in amperes (symbol A), commonly known as amps, and time is measured in seconds.

The relationship is:

$$\text{charge (coulombs)} = \text{current (amps)} \times \text{time (seconds)}$$

$$Q = I \times t$$

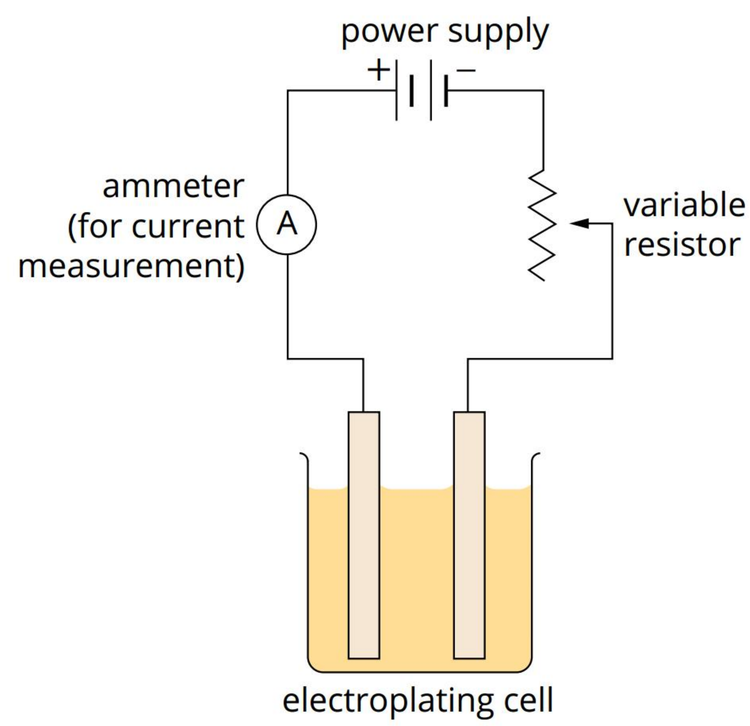


FIGURE 7.2.1 The experimental set-up used to investigate Faraday's law

Experimental data from a silver-plating cell

An electrolytic cell, shown in Figure 7.2.1, was set up to investigate the relationship between the mass of silver plated on the cathode and the amount of charge flowing through the circuit. The results from the experiment, shown in Table 7.2.1, indicate that as the charge that passes through the cell increases, more metal is formed at the cathode.

TABLE 7.2.1 The relationship between the charge and mass of silver plated on the cathode

Current	Time	Charge (C) $Q = I \times t$	Mass of silver plated (g)
2.0	200	400	0.45
2.0	400	800	0.91
2.0	600	1200	1.34
2.0	800	1600	1.79
2.0	1000	2000	2.24

Figure 7.2.2 shows a direct linear relationship between the mass of silver deposited on the cathode and the charge passed through the circuit. This is a demonstration of **Faraday's first law of electrolysis**, which can be stated as: 'The mass of a substance deposited (or the mass of gas liberated) at an electrode during electrolysis is directly proportional to the amount of charge passed through the electrolyte solution'.

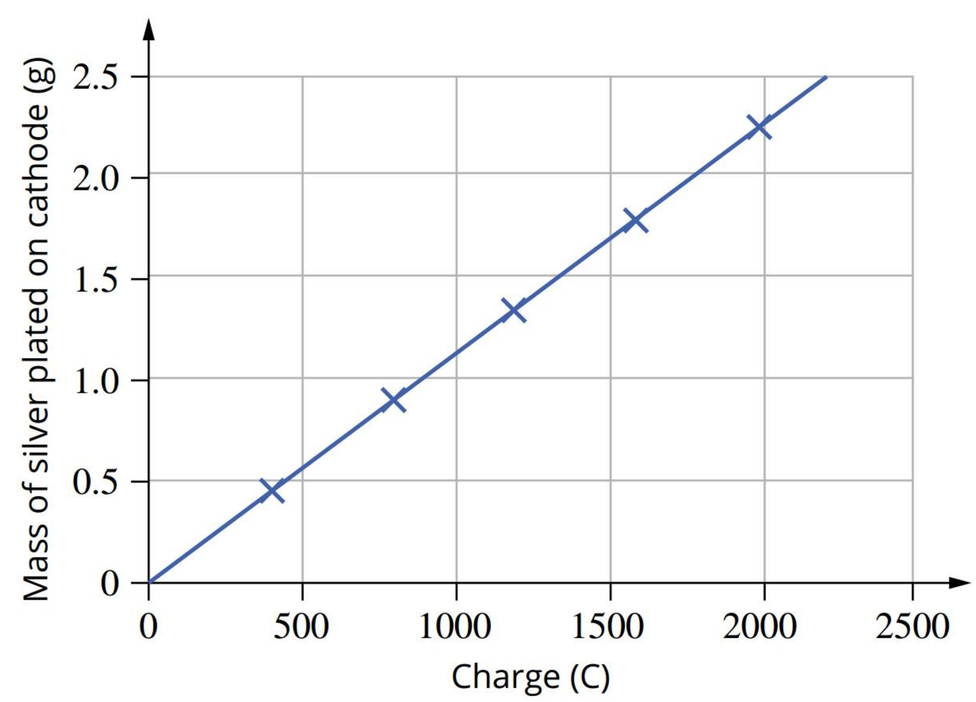


FIGURE 7.2.2 The relationship between the charge and mass of silver plated on the cathode

Faraday's first law of electrolysis can also be described mathematically as mass (m) deposited is proportional to charge passed (Q), or:

$$m \propto Q$$

Since $Q = I \times t$, can be expressed as the product of current (I) and time (t), the mass of metal deposited is also proportional to both the magnitude of the applied current (I) and the time (t) that the current is applied, i.e.:

$$m \propto I \times t$$

FARADAY'S SECOND LAW OF ELECTROLYSIS

The previous experiment can be repeated using electroplating cells for metals other than silver. Results from experiments with cells using electrolytes containing Ag^+, Cu^{2+}, Sn^{2+}, Pb^{2+} and Cr^{3+} ions are shown in the graph in Figure 7.2.3.

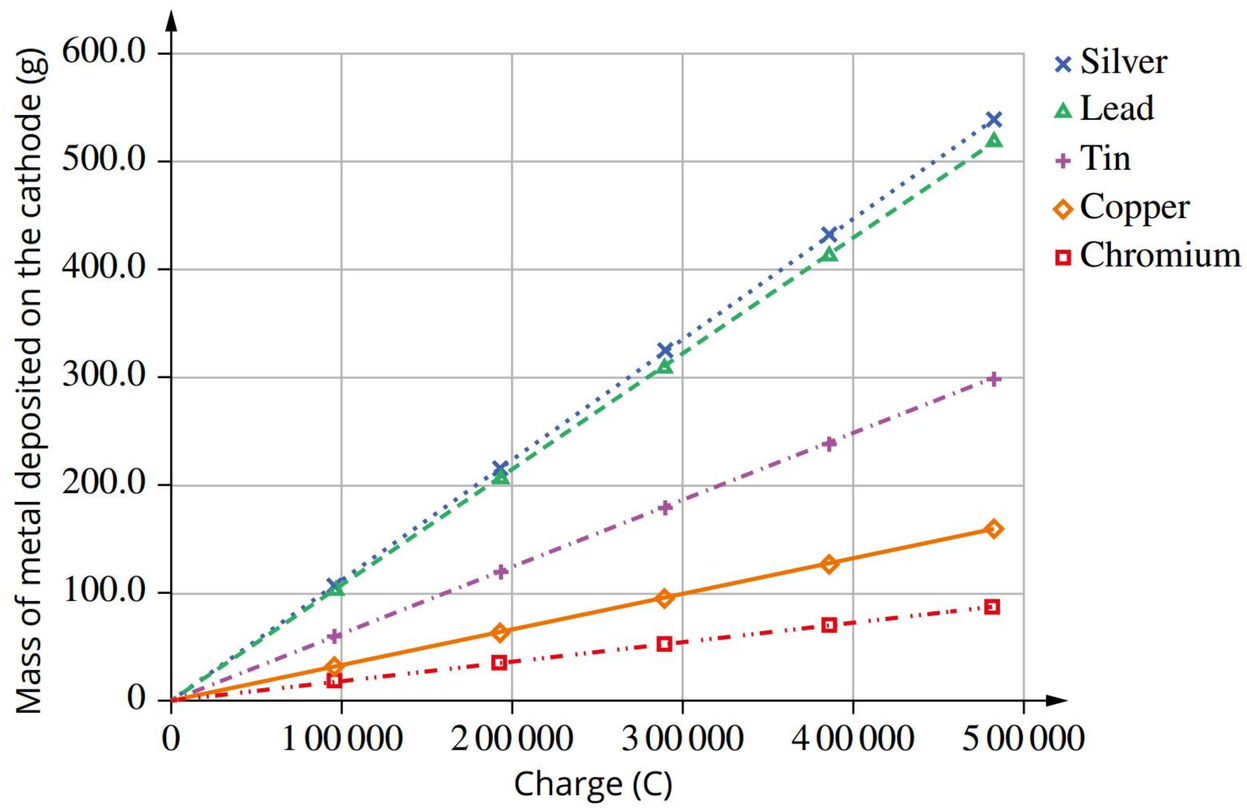


FIGURE 7.2.3 The relationship between the charge and mass of metals plated on the cathode

Although the data for each metal obeys Faraday's first law ($m \alpha Q$), at first inspection, there seems little relationship between the graphs for each metal. However, if the amount of each metal is presented as number of moles (instead of mass) plotted against charge, the results are more interesting, with Figure 7.2.4 showing that all the data points lie along just three lines, corresponding to:

- silver—where 1 mole of silver is deposited by the passage of 96 485 C (C) of charge
- copper, tin and lead—where 1 mole of each of these metals is deposited by the passage of 192 970 C of charge (which is $2 \times 96\,485$)
- chromium—where 1 mole of chromium is deposited by the passage of 289 455 C of charge (which is $3 \times 96\,485$).

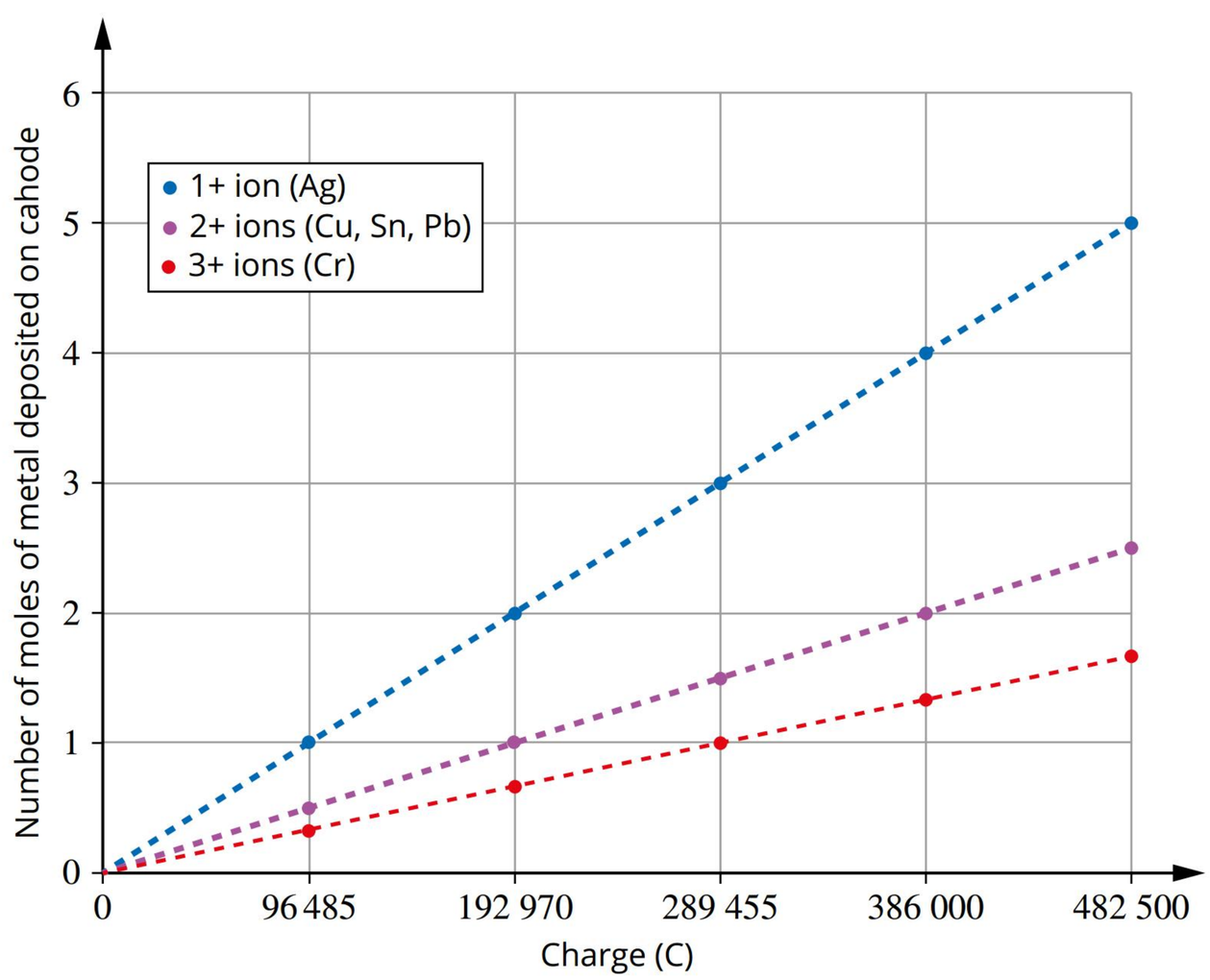


FIGURE 7.2.4 The relationship between the charge and number of moles of metals plated on the cathode for metals of different valencies

An underlying pattern is now evident.

To deposit 1 mole of silver from a solution containing Ag^+ ions, just 1 mole of electrons is required, as shown by the stoichiometry of the following reduction half-equation:

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

One mole of electrons therefore corresponds to a charge of 96 485 C.

To deposit 1 mole of copper, tin or lead from solutions of Cu^{2+}, Sn^{2+} or Pb^{2+} ions requires 2 moles of electrons, as shown by the stoichiometry of the following reduction half-equations:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$$
$$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$$

Therefore, 2 moles of electrons corresponds to a charge of 192 970 C ($2 \times 96\,485$ C).

To deposit 1 mole of chromium from solutions of Cr^{3+} requires 3 moles of electrons, as shown by the stoichiometry of the following reduction half-equation:

$$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$$

This corresponds to a charge of 289 455 C ($3 \times 96\,485$).

The charge that corresponds to the passage of 1 mole of electrons (96 485 coulombs per mole of substance) is a constant value referred to as a **Faraday's constant,** and has the symbol F with units of C mol^{-1} (coulombs per mole). Therefore, 1 $F = 96\,485$ C mol^{-1}.

The charge on a given number of moles of electrons, $n(e^-)$, can be readily calculated. For example, 2 moles of electrons have a charge of 192 970 C. We can express this mathematically by:

$$Q = n(e^-) \times F$$
$$\text{or } Q = n(e^-) \times 96\,485$$

where Q is the charge (C), $n(e^-)$ is the number of moles of electrons transferred in the redox reaction and F is Faraday's constant (96 485 C mol^{-1}).

The three different slopes of the lines on the graph in Figure 7.2.4 arise because of the different charges on the metal ions and the fact that number of moles (not mass) of deposited metal are plotted against charge. These experimental results give rise to **Faraday's second law of electrolysis**, which can be stated as: 'The mass of a substance liberated or deposited during electrolysis is proportional to the molar mass divided by the charge on the ion in the balanced half equation'. Faraday's second law can also be expressed as follows: to produce 1 mole of metal during electrolysis, 1, 2, 3 or another whole number of moles of electrons must be consumed.

Although Faraday's laws were developed by studying the deposition of metals at the cathode in electroplating cells, the laws apply just as well to the production or consumption of any substance at the surface of electrodes in either electrolytic cells or galvanic cells. Corresponding coulometric calculations are based on the two relationships developed in this module, namely:

$$Q = I \times t$$
$$Q = n(e^-) \times F$$

CALCULATIONS USING FARADAY'S LAWS

Worked example 7.2.1 shows you how to calculate the mass of a chemical produced at an electrode of an electrolytic cell.

Worked example 7.2.1

CALCULATING THE MASS OF A PRODUCT AT AN ELECTRODE

A chromium-plating cell operates with a steady current of 30.0 A for 20.0 minutes. What mass of chromium is plated on the object at the cathode? The equation for the reaction is:

$$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$$

Thinking	Working
Calculate the quantity of charge passing through a cell using the formula: $Q = I \times t$ Remember that time must be expressed in seconds.	$Q = I \times t$ $= 30.0 \times 20.0 \times 60$ $= 3.60 \times 10^4$ C
Calculate the number of moles of electrons that passed through the cell using the formula: $Q = n(e^-) \times F$ Recall that F = 96485 C.	Rearrange to find $n(e^-)$: $n(e^-) = \frac{Q}{F}$ $= \frac{3.60 \times 10^4}{96485}$ $= 0.373$ mol
Use the mole ratio from the equation for the reaction to determine the number of moles of chromium plated at the cathode.	The cathode reaction is: $Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$ 3 moles of electrons will deposit 1 mole of chromium metal. Mole ratio: $\frac{n(Cr)}{n(e^-)} = \frac{1}{3}$ $n(Cr) = \frac{1}{3} \times n(e^-)$ $= \frac{1}{3} \times 0.373$ $= 0.124$ mol
Calculate the mass of chromium plated at the cathode.	The molar mass of Cr is 52.0 g mol^{-1}. $m(Cr) = n(Cr) \times M$ $= 0.124 \times 52.00$ $= 6.45$ g

➤ Try yourself 7.2.1

CALCULATING THE MASS OF A PRODUCT AT AN ELECTRODE

A copper-plating cell operates with a steady current of 20.0 A for 15.0 minutes. What mass of copper is plated on the object at the cathode? The equation for the reaction is:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

Faraday's laws can also be used to determine the time it would take to produce a specific mass of product at an electrode.

Worked example 7.2.2

CALCULATING THE TIME TAKEN TO PRODUCE A PRODUCT AT AN ELECTRODE

How long would it take, in hours, to deposit 50.0 g of copper at the cathode of a copper-plating cell operating at a current of 8.00 A? The half-equation for the reaction is:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

Thinking	Working
Calculate the number of moles of a substance that was deposited or consumed at the electrode using the formula: $n = \frac{m}{M}$	$n(Cu) = \frac{m}{M}$ $= \frac{50.0}{63.55}$ $= 0.787$ mol
Calculate the number of moles of electrons that must have passed through the cell using the mole ratio from the equation for the reaction.	The cathode reaction is: $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ 2 moles of electrons will deposit 1 mole of copper metal. $\frac{n(e^-)}{n(Cu)} = \frac{2}{1}$ $n(e^-) = 2 \times n(Cu)$ $= 2 \times 0.787$ $= 1.57$ mol
Determine the quantity of charge that passed through the cell using the formula: $Q = n(e^-) \times F$ Recall that $F = 96\,485$ C.	$Q = n(e^-) \times F$ $= 1.57 \times 96\,485$ $= 1.51 \times 10^5$ C
Use the formula $Q = I \times t$ to determine the length of time the current must flow to deliver that quantity of charge to the cell.	Rearrange $t = \frac{Q}{I}$ $= \frac{1.51 \times 10^5}{8.00}$ $= 1.89 \times 10^4$ s
Convert seconds to hours by dividing by 60 × 60.	$t = \frac{1.89 \times 10^4}{60 \times 60}$ $= 5.25$ h

➤ Try yourself 7.2.2

CALCULATING THE TIME TAKEN TO PRODUCE A PRODUCT AT AN ELECTRODE

How long would it take, in hours, to deposit 20.0 g of silver at the cathode of a silver-plating cell operating at a current of 6.50 A? The half-equation for the reaction is:

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$$

Faraday's laws also apply to other redox equations, for instance, fuel cells.

Worked example 7.2.3

CALCULATING THE TIME TAKEN TO USE A FIXED MASS OF FUEL IN A FUEL CELL

A fuel cell uses ethanol (C_2H_5OH) as its fuel source. How long would it take, in seconds, for 200 g of ethanol to be used in the fuel cell operating at a current of 1.25 A? The half-equation for the reaction is:

$$C_2H_5OH(l)+3H_2O(l) \rightarrow 2CO_2(g)+12H^+(aq)+12e^-$$

Thinking	Working
Calculate the number of moles of ethanol used in the fuel cell using the formula: $n(C_2H_5OH) = \frac{m}{M}$	$n(C_2H_5OH) = \frac{m}{M}$ $= \frac{200}{46.08}$ $= 4.34$ mol
Use the mole ratio from the equation for the reaction to determine the number of moles of electrons produced in the reaction per mole of ethanol reacted.	The reaction is: $C_2H_5OH(l)+3H_2O(l) \rightarrow 2CO_2(g)+12H^+(aq)+12e^-$ 12 moles of electrons are produced for every 1 mole of ethanol that reacts. Mole ratio: $\frac{n(e^-)}{n(C_2H_5OH)} = \frac{12}{1}$ $n(e^-) = 12 \times n(C_2H_5OH)$ $= 12 \times 4.34$ $= 52.08$ mol
Calculate the quantity of charge generated by the fuel cell using the formula: $Q = n(e^-) \times F$ Recall that $F = 96\,485$ C.	$Q = n(e^-) \times F$ $= 52.08 \times 96\,485$ $= 5.02 \times 10^6$ C
Calculate the time taken to use the ethanol using the formula: $Q = I \times t$	Rearrange to find t: $t = \frac{Q}{I}$ $= \frac{5.02 \times 10^6}{1.25}$ $= 4.02 \times 10^6$ s

➤ Try yourself 7.2.3

CALCULATING THE TIME TAKEN TO USE A FIXED MASS OF FUEL IN A FUEL CELL

A fuel cell uses propanal, CH_3CH_2CHO, as its fuel source. How long would it take, in seconds, for 375 g of propanal to be used in the fuel cell operating at a current of 5.40 A? The half-equation for the reaction is:

$$CH_3CH_2CHO(l)+5H_2O(l) \rightarrow 3CO_2(g)+16H^+(aq)+16e^-$$

As you have seen in this chapter, gases are often evolved from electrodes during electrolysis. The volume of the gases, just like masses, is related to the charge passed through the electrolytic cell and can be calculated from the gas laws covered in Unit 2.

Worked example 7.2.4

CALCULATING THE VOLUME OF A GAS PRODUCED IN AN ELECTROLYTIC CELL

Water is electrolysed by passing a current of 10.0 A through a cell for 45.0 minutes.

Calculate the volume of gas, in L, measured under STP, formed at each electrode after 45.0 minutes.

Thinking	Working
Determine the charge passing through the cell using the formula: $Q = I \times t$	$Q = I \times t$ $= 10.0 \times 45.0 \times 60$ $= 27\,000\,\text{C}$
Write the half-reactions occurring at each electrode. Identify the reactions in the cell.	$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $-0.83\,\text{V}$ $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $+1.23\,\text{V}$
Determine the number of moles of electrons transferred in the cell using the formula: $n(e^-) = \frac{Q}{F}$ Recall that $F = 96\,485\,\text{C}$.	$n(e^-) = \frac{Q}{F}$ $= \frac{27\,000}{96\,485}$ $= 0.280\,\text{mol}$
Write the reaction at the cathode.	$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$
Using the mole ratio of $H_2(g)$: e^- from the balanced chemical equation, calculate the number of moles of hydrogen formed.	$n(H_2) = \frac{n(e^-)}{2}$ $= \frac{1}{2} \times 0.280\,\text{mol}$ $= 0.140\,\text{mol}$
Write the reaction at the anode.	$2H_2O(l) \rightleftharpoons O_2(g) + 4H^+(aq) + 4e^-$
Using the mole ratio of $O_2(g)$: e^- from the balanced chemical equation, calculate the number of moles of oxygen formed.	$n(O_2) = \frac{n(e^-)}{4}$ $= \frac{1}{4} \times 0.280\,\text{mol}$ $= 0.0700\,\text{mol}$
Calculate the volume of gas formed using the formula: $V_n = n \times \text{molar volume at STP}$	$V_n = n \times \text{molar volume at STP}$ $V_{H_2} = 0.140 \times 2.27 \times 10^{-2}\,\text{m}^3$ $= 0.00318\,\text{m}^3$ $V_{O_2} = 0.0700 \times 2.27 \times 10^{-2}\,\text{m}^3$ $= 0.00159\,\text{m}^3$

➤ Try yourself 7.2.4

CALCULATING THE VOLUME OF A GAS PRODUCED IN AN ELECTROLYTIC CELL

When molten copper(II) chloride is electrolysed, chlorine gas is formed at the anode.

Calculate the volume of chlorine gas produced at STP by passing a current of 13.0 A through a cell for 600 seconds.

7.2 Review

SUMMARY

- The charge passing through an electrochemical cell can be calculated from the formula:
  Charge (coulombs) = current (amps) × time (seconds)
  $$Q = I \times t$$
- Faraday's first law states that the amount of a substance deposited or mass of gas liberated at a particular electrode is directly proportional to the amount of charge passing through the solution.
- Faraday's second law states that the mass of different substances liberated or deposited by the same quantity of electricity is proportional to the molar masses divided by the valency of their ions.
- The charge on 1 mole of electrons is represented by the Faraday constant (F), where
  $1\,F = 96\,485\,C\,mol^{-1}$.
- The charge on a quantity of electrons can be calculated from:
  Charge = number of moles of electrons × F
  $$Q = n(e^-) \times F$$
- Faraday's laws can be used to calculate the:
  - mass of a reactant consumed or product formed in a cell, given the current and the operating time
  - current passing through a cell, given the mass of the reactant consumed or product formed and the operating time
  - time required for a cell to operate, given the mass of the reactant consumed or product needed and the current through the cell.

KEY QUESTIONS

Describe

1 State Faraday's first law of electrolysis.

2 What is the relationship between current and charge?

Apply

3 How many moles of electrons are required to reduce 0.5 moles of aluminium ions?

4 What quantity of charge is required to reduce 1.7 moles of calcium ions?

5 0.75 moles of zinc are formed when a current is passed through a zinc chloride solution for 10 minutes. If the same current is passed through an aluminium nitrate solution for 5 minutes, how many moles of aluminium are formed?

Analyse

6 Determine the mole ratio of electrons to metal, $\frac{n(e^-)}{n(M^+)}$, in the following experiment.

A current of 5.00 A was passed through an electrolytic cell for 15.0 minutes and 0.023 moles of the metal formed.

7 What amount of charge is required to produce 0.650 mol of oxygen at STP from the electrolysis of dilute sulfuric acid?

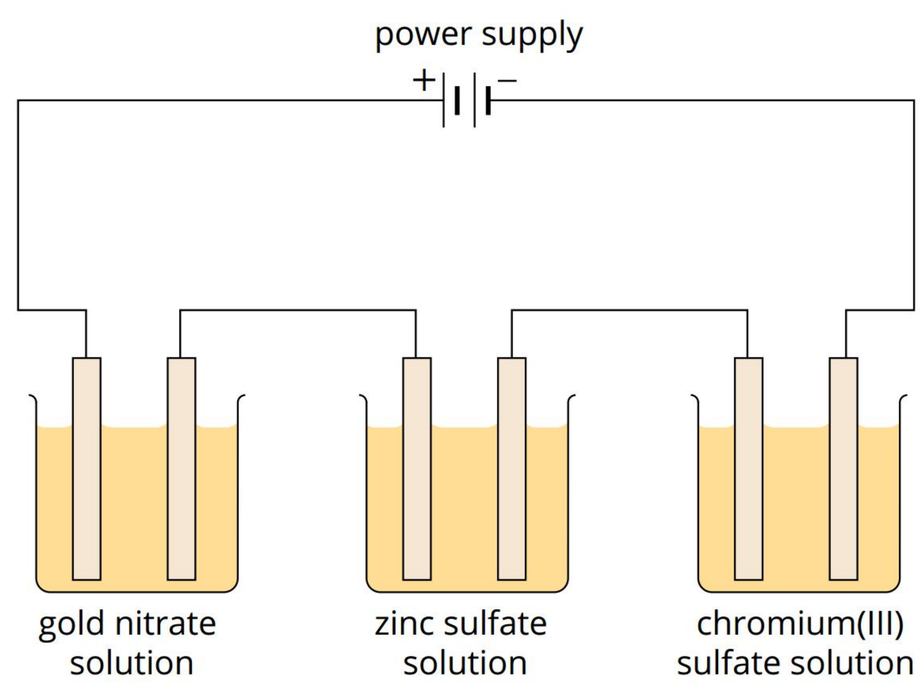
8 A charge of 38 600 C was passed through 1.00 L of 1.00 M copper(II) sulfate solution using carbon electrodes.

a Write half-equations for the reactions that occur at each electrode.

b Calculate the concentration of the copper(II) ions in solution after electrolysis. Assume no change in the volume of the electrolyte.

9 A thin layer of silver is to be plated onto a piece of jewellery in a solution of silver nitrate, using a current of 2.00 A. How long would it take to plate 5.00 g of silver?

10 Three electrolytic cells containing gold(I) nitrate solution, zinc sulfate solution and chromium(III) sulfate solution, respectively, were connected in series so that the same amount of electric charge passed through each cell (see the figure below). Metal was deposited at the cathode of each cell.



a Write half-equations for the reduction reaction that occurs in each cell.

b If 15.0 g of gold was obtained from one cell, what mass of metal, in g, would be obtained from each of the other cells?

Chapter review

07

KEY TERMS

anode
cathode
coulomb
electrolysis
electrolyte
electroplating
electrorefining
Faraday's constant
Faraday's first law of electrolysis
Faraday's second law of electrolysis
inert
inert electrode
molten
non-spontaneous reaction
reactive electrode
smelting
standard electrode potential

KEY QUESTIONS

Describe

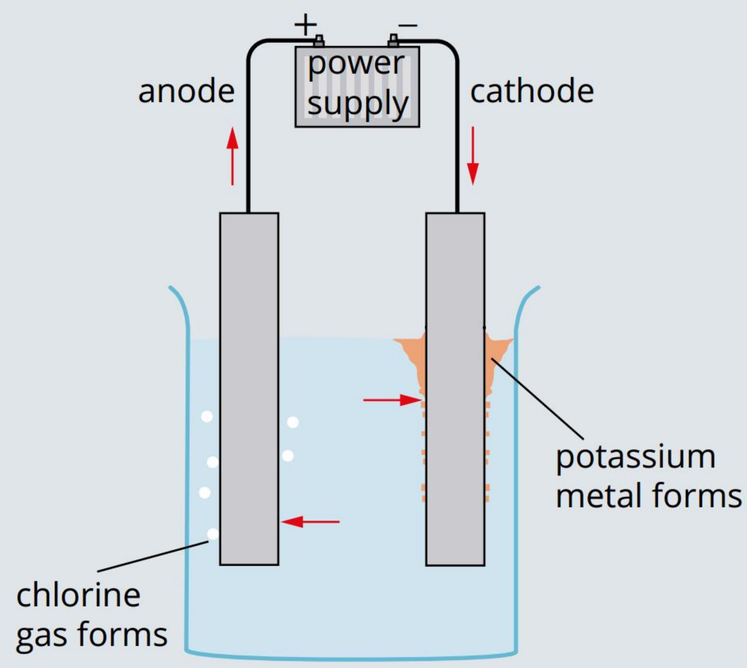
1 Identify which one of the following options applies to both galvanic and electrolytic cells.

A Both cells have non-spontaneous reactions.
B The anode is negative and the cathode is positive.
C Both cells convert chemical energy into electrical energy.
D Oxidation occurs at the anode and reduction occurs at the cathode.

2 For both electrolytic and galvanic cells, recall the:

a polarity of the anode and cathode
b direction of electron flow
c energy transformation occurring in the cells
d tendency of the cell reaction to occur spontaneously.

3 The electrochemical cell shown below is set up to produce potassium metal. Identify the parts of the cell using the following labels (labels may be used more than once): Cl^-, molten potassium chloride, platinum, K^+.



Apply

4 Identify the products of electrolysis of molten potassium iodide using inert electrodes.

A Iodine at the anode and hydrogen at the cathode.
B Potassium at the anode and iodine at the cathode.
C Potassium at the cathode and iodine at the anode.
D Iodine at the negative electrode and potassium at the positive electrode.

5 Explain why Mg cannot be extracted from a dilute magnesium chloride solution by electrolysis.

6 Determine the amount of charge required to reduce 2.5 moles of $Mn^{2+}(aq)$ to Mn.

7 Calculate the time in hrs required to produce 4.00 dm^3 of gas at STP when aluminium chloride is electrolysed using 4.00 A.

8 What is the minimum voltage required to form nickel from an aqueous solution of $Ni(OH)_2$ using inert electrodes?

Analyse

9 State the electrode reactions and overall reaction when molten $ZnCl_2$ is used as the electrolyte in an electrolytic cell with inert electrodes.

10 Two electrolytic cells were set up for the electrolysis of aqueous copper(II) sulfate. One cell contained copper electrodes and the other contained platinum electrodes. Determine the reactions that would occur at the electrodes of both cells.

11 An aqueous zinc sulfate solution was electrolysed using copper electrodes.

a Refer to the table of standard electrode potentials (Table 2 in Appendix E) and identify the possible reactions that could occur. Write these half-equations in the order they appear in the series.
b Identify the half-equations for the reactions that occur at the anode and cathode.
c Write an equation for the overall reaction.

12 Using the table of standard electrode potentials (Table 2 in Appendix E), predict the products of each of the following electrolysis experiments by completing the following table.

Experiment	Electrolyte	Electrodes	Cathode reaction	Anode reaction
a	molten potassium iodide	platinum		
b	copper(II) sulfate solution	platinum		
c	potassium bromide solution	copper		
d	a mixture of copper(II) nitrate and nickel(II) nitrate solutions	carbon		
e	lithium fluoride solution	platinum		

13 Sodium and chlorine are manufactured by passing direct current through molten sodium chloride. Determine why it is necessary for the electrolyte to be molten and not aqueous.

14 When constructing a galvanic cell in the laboratory, explain why two half-cells are usually used, whereas the reactants of an electrolytic cell are often placed in a single container.

15 A cell was set up, and a 5.0 A current was passed through the platinum electrodes for 10 minutes. When the power supply was switched off, the mass of the cathode had increased by 0.54 g.

The chemist knew that the electrolyte was one of the following solutions: $AgNO_3$, $Cd(NO_3)_2$, $Pb(NO_3)_2$ or $Cr(NO_3)_3$.

Which solution was used in the cell?

16 Determine the mass of zinc consumed in an alkaline battery used in a torch that has been turned on for 1.20 hours and draws a current of 0.450 A.

17 The electrolysis of a metal salt using 1.20 A for 30 minutes produces a deposit of 0.0110 moles of a metal. Determine the charge on the metal ion.

Interpret

18 Design a cell that would allow magnesium metal to be electroplated onto an iron electrode. Draw and fully label a diagram of your cell.

19 Create a concept map that includes the following terms: electrolysis, electrolytic cell, chemical energy, electrical energy, anode, cathode, reducing agent, oxidising agent, reduction, oxidation, electrolyte, non-spontaneous reactions.

20 A dilute solution of sodium chloride is electrolysed using inert electrodes.

Explain what would happen to the colour of the solution around the positive and negative electrodes when a couple of drops of phenol red were added at each electrode. Use half-cell reactions to support your explanation.

Data analysis

DATA SET 1

The information below applies to Questions 1–4.

To investigate Faraday's first law of electrolysis, a student plated a nickel medallion with copper using 250 mL of 1.00 M copper(II) sulfate solution with a large copper anode. Each experiment uses the same medallion that is dried and reweighed before each test. Other conditions are kept constant.

Each experiment ran for 20 minutes with a different current. The results are shown in the table.

Current (A)	Mass of copper deposited on the nickel medallion (g)
2.0	0.753
4.0	1.508
6.0	2.251
8.0	3.001
10.0	3.754

Question 1 (2 marks)

Write an aim for this investigation.

Question 2 (2 marks)

Identify the independent and dependent variables in the investigation.

Question 3 (5 marks)

Determine the theoretical mass of copper, in g, plated onto the medallion in the experiment with a current of 10.0 A.

Question 4 (2 marks)

Calculate the concentration of copper(II) sulfate at the end of the experiment. Assume there is no change in the volume of the electrolyte.

UNIT 3 • REVIEW

REVIEW QUESTIONS

Equilibrium, acids and redox reactions

Topic 1: Chemical equilibrium systems

Multiple choice

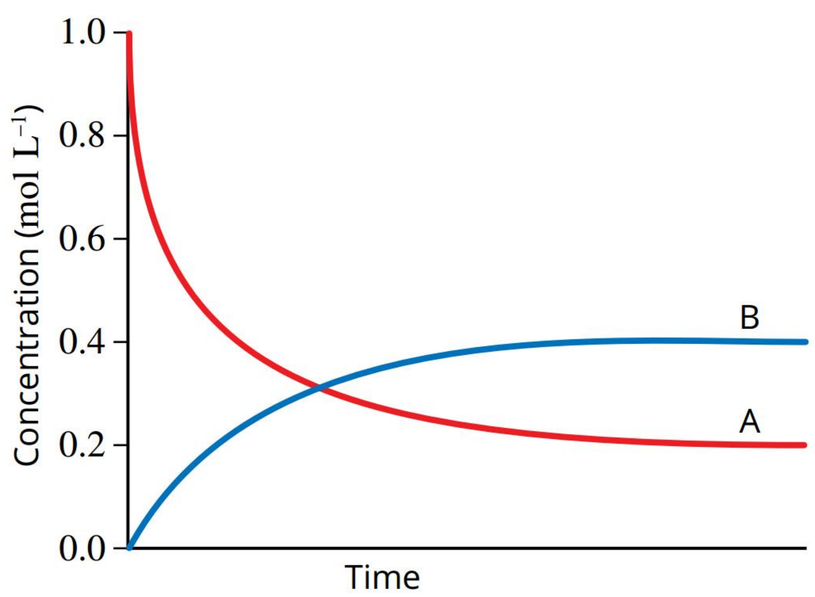
1 Identify the statement that correctly describes a closed system. In a closed system:

A only matter is exchanged with the surroundings.
B only energy is exchanged with the surroundings.
C both matter and energy are exchanged with the surroundings.
D neither matter nor energy is exchanged with the surroundings.

2 Select an example that involves a reversible chemical reaction.

A an electric car powered by a fuel cell
B the rechargeable battery in a mobile phone
C the combustion of a fuel to produce heat for cooking
D the setting of a dental filling

3 Examine the following concentration–time graph.



Identify the equation represented by this graph.

A $A \rightleftharpoons B$
B $B \rightleftharpoons A$
C $2A \rightleftharpoons B$
D $A \rightleftharpoons 2B$

4 In a sealed vessel, nitrogen monoxide, oxygen and nitrogen dioxide gases exist together in the following equilibrium.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = -114\,kJ\,mol\,L^{-1}$$

Identify the set of conditions likely to give the highest yield of nitrogen dioxide gas.

A 200°C and 100 kPa
B 200°C and 200 kPa
C 300°C and 100 kPa
D 300°C and 200 kPa

5 A sample of nitrosyl chloride (NOCl) is allowed to come to equilibrium according to the following equation.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

The volume of the mixture is halved, and it is allowed to come to a new equilibrium with the temperature remaining constant. Predict how the number of moles and the concentration of chlorine have changed at the new equilibrium.

A number of moles has decreased in amount and decreased in concentration
B number of moles has increased in amount and decreased in concentration
C number of moles has decreased in amount and increased in concentration
D number of moles has increased in amount and increased in concentration

6 Carbon dioxide gas dissolves to a small extent in water, forming carbonic acid in an exothermic reaction. This is the reaction involved in forming fizzy drinks. The carbonic acid can act as a weak acid in water.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \quad \Delta H \text{ negative}$$
$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

Predict which one of the following strategies would not be effective at increasing the amount of dissolved carbon dioxide.

A decreasing the pH of the solution
B decreasing the temperature of the solution
C increasing the pressure of the carbon dioxide gas
D increasing the concentration of carbon dioxide in the gas

7 Consider the following equation.

$$A + 3B \rightleftharpoons 2C + 4D$$

Select the correct expression for the equilibrium constant.

A $\dfrac{[A][3B]^3}{[2C]^2[4D]^4}$

B $\dfrac{[C]^2[D]^4}{[A][B]^3}$

C $\dfrac{[A][B]^3}{[C]^2[D]^4}$

D $\dfrac{[2C][4D]}{[A][3B]}$

8 The reaction between nitrogen monoxide and ozone is:

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$
$$K = 6 \times 10^{34} \text{ at } 25°C$$

Equal amounts of NO and O_3 are used. Identify which of the following statements cannot be inferred from the magnitude of the equilibrium constant.

A At equilibrium, $[NO_2][O_2] >> [NO][O_3]$.
B The reaction has a low activation energy.
C Very little ozone will remain at equilibrium.
D The equilibrium of the reaction lies well to the right.

9 At equilibrium, the reaction shown below has a ratio of atoms A:B of 2:3.

$$A(g) \rightleftharpoons B(g) \quad \Delta H > 0$$

The equilibrium mixture is heated. Describe the most likely ratio of atoms in the new equilibrium mixture.

A no change
B 3:2
C 2:3
D 2:6

10 Mercury(I) chloride has a very low solubility in water. The equation for the reaction is:

$$Hg_2Cl_2(s) \rightleftharpoons 2Hg^+(aq) + 2Cl^-(aq)$$

The K_{sp} expression for this reaction is:

A $K_{sp} = [Hg^+][Cl^-]$
B $K_{sp} = [2Hg^+][2Cl^-]$
C $K_{sp} = [Hg+]^2[Cl^-]^2$
D $K_{sp} = [Hg^+][Cl^-]^2$

11 Compare 0.1 mol L^{-1} solutions of HNO_3, HNO_2 and H_2SO_4. The K_a values for the acids are:

$K_a(HNO_3) = 25$
$K_a(HNO_2) = 7 \times 10^{-4}$
$K_a(H_2SO_4) = 10^9$

Identify the statement that correctly describes the properties of these acids.

A A solution of 0.1 mol L^{-1} HNO_3 has a higher pH than a solution of 0.1 mol L^{-1} H_2SO_4.
B A 20.0 mL solution of 0.1 mol L^{-1} HNO_2 has a higher pH than a 10.0 mL solution of 0.1 mol L^{-1} HNO_2.
C A 10.0 mL solution of 0.1 mol L^{-1} HNO_3 will require a greater volume of 0.2 mol L^{-1} NaOH solution for its neutralisation than a 10.0 mL solution of 0.1 mol L^{-1} HNO_2.
D A 0.1 mol L^{-1} solution of HNO_3 will produce a greater volume of hydrogen at STP on reaction with excess magnesium than the same volume of 0.1 mol L^{-1} HNO_2.

12 Identify the dilute solution of a strong acid.

A 6.0 mol L^{-1} HNO_3
B 0.10 mol L^{-1} HNO_3
C 8.0 mol L^{-1} CH_3COOH
D 0.01 mol L^{-1} CH_3COOH

13 The pH of a 0.01 mol L^{-1} aqueous sodium hydroxide is:

A equal to 2.
B equal to 7.
C equal to 12.
D between 7 and 11.

14 Four beakers contain samples of acid as described below.

Beaker I: 10 mL of 0.0001 mol L^{-1} HCl
Beaker II: 10 mL of 5.0 mol L^{-1} HCl
Beaker III: 2500 mL of 0.01 mol L^{-1} HCl
Beaker IV: 2500 mL of 5.0 mol L^{-1} HCl

Identify the beaker(s) that contains the solution that has the highest pH.

A I only
B II only
C I and III only
D II and IV only

15 Identify the conjugate acid formed in the hydrolysis of the carbonate ion, CO_3^{2-}, in aqueous solution.

A H_3O^+
B CO_3^{2-}
C HCO_3^-
D $H_2CO_3^-$

16 Select the reaction in which water is acting as a Brønsted–Lowry acid.

A $H_2O(l) + NH_3(g) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
B $H_3O^+(aq) + HS^-(aq) \rightleftharpoons H_2S(aq) + H_2O(l)$
C $H_2O(l) + HCO_3^-(aq) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$
D $2Na(s) + 2H_2O(l) \rightleftharpoons 2Na^+(aq) + 2OH^-(aq) + H_2(g)$

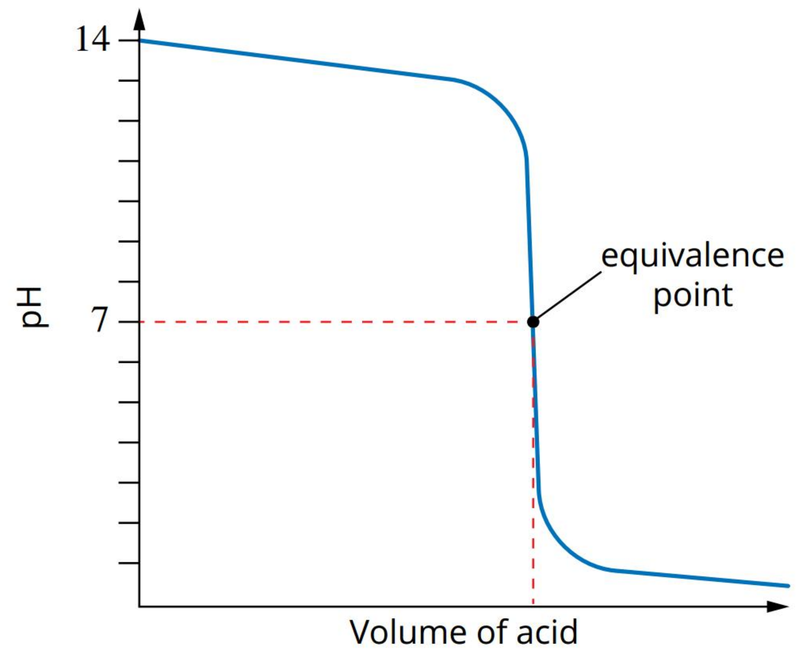
17 Select the correct statement about the use of indicators in acid–base titrations.

A Indicators are coloured compounds that are strong acids or bases.
B Phenolphthalein is a good indicator for all titrations because its colour change is so distinctive.
C Acid–base indicators must change colour at pH 7 when the acid and base have neutralised each other.
D An indicator should change colour at the point when the reactants are in the mole ratio indicated in the reaction equation.

18 The equivalence point in an acid–base titration is when:

A the amount of acid equals the amount of base.
B the indicator changes colour.
C the amounts of acid and base are present in the ratio of the balanced equation.
D the volumes of acid and base used are equal.

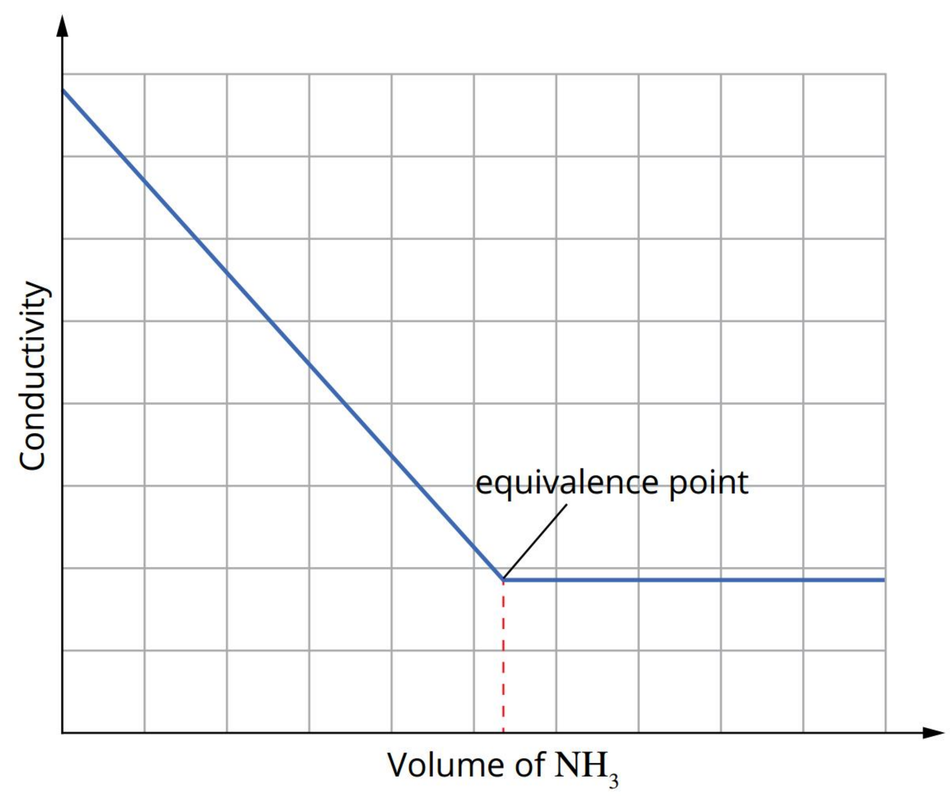
19 The pH curve for a titration is shown below.



This curve could represent the addition of:

A ethanoic acid to sodium hydroxide solution.
B hydrochloric acid to sodium hydroxide solution.
C ethanoic acid to ammonia solution.
D sodium hydroxide to ethanoic acid solution.

20 The conductivity curve for a titration is shown below.



This curve could represent the addition of:

A hydrochloric acid to sodium hydroxide solution.
B hydrochloric acid to ammonia solution.
C ammonia to hydrochloric acid solution.
D sodium hydroxide to hydrochloric acid solution.

21 A 50.0 mL sample of solution of silver nitrate, $AgNO_3$, is added to a small beaker and electrodes attached to a power supply are placed in the beaker to record the electrical conductivity of the solution.

KBr solution is added to this beaker from a burette, leading to the formation of a precipitate of AgBr.

In this experiment, the electrical conductivity:

A will increase with each addition because of the extra ions added.
B will decrease and then increase at a different rate.
C will drop to zero and then increase at the same rate.
D will drop to zero and then remain at zero.

Short answer

1 The three phases of water, when in a sealed container at 0.1°C and 610 Pa, exist in a stable equilibrium. This is known as the triple point of water.

a Write equations that demonstrate the equilibrium at the triple point between:
i ice and water
ii water and water vapour
iii ice and water vapour.

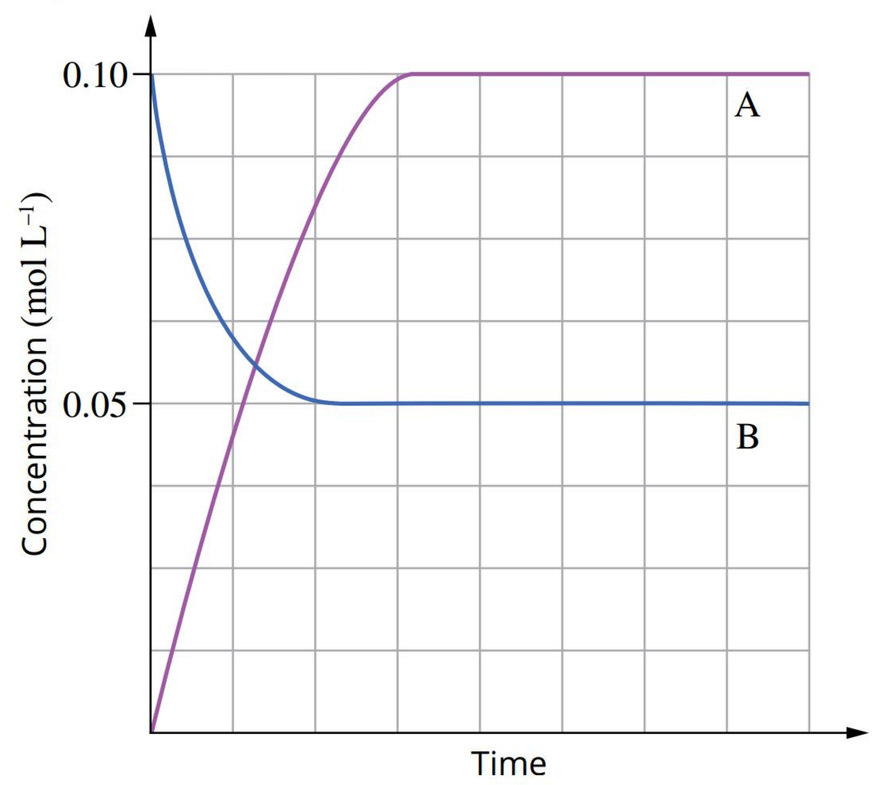
b State why these are considered to be physical reactions.

c At 2000°C, water decomposes into its constituent elements.
i Construct a balanced equation for this reaction.
ii State why this is considered to be a chemical reaction.

2 The gases dinitrogen tetroxide (N_2O_4) and nitrogen dioxide (NO_2) coexist according to the following equilibrium reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

A concentration–time graph for the system coming to equilibrium is shown below.



a Identify A and B.

b Construct an expression for the equilibrium constant of the decomposition of N_2O_4.

c Copy the graph and sketch a line showing the effect on A if a catalyst had been present in the mixture from the beginning.

d Calculate K_c for the reaction at equilibrium according to this concentration graph.

3 Carbon monoxide and iodine pentoxide react to form iodine and carbon dioxide in the following equilibrium reaction:

$$5CO(g) + I_2O_5(s) \rightleftharpoons I_2(g) + 5CO_2(g) \quad \Delta H = -1175\,kJ$$

Using your knowledge of Le Châtelier's principle, copy and complete the following table by predicting the effect the change (column 1) will have on the quantity (column 2). Assume that the change listed is the only one taking place (e.g. if I_2 is added, the volume and the temperature are kept constant).

	Change	Quantity	Increase/ decrease/ no change
a	increase T	K_c	
b	decrease T	amount $I_2O_5(s)$	
c	add $I_2(g)$	K_c	
d	add $CO_2(g)$	amount $I_2(g)$	
e	double volume	amount $CO_2(g)$	
f	double volume	concentration $CO_2(g)$	
g	remove CO(g)	amount $CO_2(g)$	
h	add catalyst	amount $I_2(g)$	
i	add inert gas (Ar)	K_c	

4 A student is given the task of reducing the concentration of free metal ions in various aqueous samples using ammonia solution. Ammonia is capable of reacting with metal ions and forming complex ions. The student adds the same volume of ammonia solution (an excess) to each test tube initially containing 0.1 mol L^{-1} solutions of the metal ions. The information about each reaction is shown below.

Test tube	Metal ion	Equilibrium reaction	Equilibrium constant
1	Cd^{2+}	$Cd^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cd(NH_3)_4{}^{2+}(aq)$	1×10^7
2	Cu^{2+}	$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq)$	1×10^{13}
3	Zn^{2+}	$Zn^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Zn(NH_3)_4{}^{2+}(aq)$	1×10^9

Explain which of the three test tubes will contain the smallest concentration of 'free' metal ions.

5 The pH and electrical conductivity of four different mixtures were measured, as shown in the following table.

Mixtures	Conductivity (mA)	pH
A 0.1 mol L^{-1} HCl	260	1
B 0.1 mol L^{-1} CH_3COOH	5	3
C Mixture made by mixing equal volumes of 0.2 mol L^{-1} HCl and 0.2 mol L^{-1} NaCl	340	1
D Mixture made by mixing equal volumes of 0.2 mol L^{-1} HCl and 0.2 mol L^{-1} $NaCH_3COO$	80	3

a State why the conductivity of mixture A is higher than the conductivity of mixture B, yet the pH of A is lower than the pH of B. Include relevant equations in your answer.

b State why the pH of mixture C is the same as the pH of mixture A.

c State why the conductivity of mixture C is higher than the conductivity of mixture A.

d State why the pH of mixture D is the same as the pH of mixture B.

6 The pH of three different acids is given below.

Acid	Concentration (mol L^{-1})	pH
nitric acid (HNO_3)	0.010	2.0
propanoic acid (C_2H_5COOH)	0.010	3.4
sulfuric acid (H_2SO_4)	0.010	1.7

The three acids have the same concentration. Explain why:

a propanoic acid has the highest pH of the three acids

b sulfuric acid has the lowest pH of the three acids.

7 **a** Represent the self-ionisation of water as an equation.

b The temperature of water placed in the refrigerator decreases to about 4°C. At this temperature, the value of the equilibrium constant for the reaction from part **a**, K_w, is 1.2×10^{-15}. Calculate the pH of pure water at 4°C using this information.

c Predict whether pure water at 4°C is neutral, acidic or basic. Explain your answer.

8 **a** A solution has a pH of 5.2. Calculate:

i the concentration, in mol L^{-1}, of hydroxide ions in the solution at 25°C

ii the pOH of the solution.

b 75 mL of a 0.0150 mol L^{-1} solution of hydrochloric acid is added to 125 mL of a 0.0100 mol L^{-1} solution of sodium hydroxide. Both solutions are at 25°C. Calculate the pH of the resultant solution.

9 The concentration of a solution of ammonium chloride was determined by titration against a standard solution of sodium hydroxide. The sodium hydroxide solution was placed in a burette, and the ammonium chloride solution was pipetted into a conical flask.

Identify the solution or liquid you would use to rinse the following pieces of equipment just prior to use.

Equipment	Wash with
burette	
pipette	
conical flask	

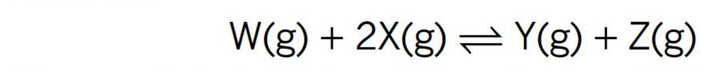
10 A chemistry class was asked to prepare a solution of a primary standard to titrate against a solution of hydrochloric acid. In response to this task, a student carried out the following procedure.

The student used sodium hydroxide solution as the primary standard, since they knew that sodium hydroxide and hydrochloric acid react. The student obtained a 500.00 mL volumetric flask, which looked dirty, so the student rinsed it out with detergent and hot tap water.

The student weighed out 4.321 g of sodium hydroxide pellets on a watch glass and transferred the pellets into the volumetric flask by gently tapping the watch glass. Then, using a 50.00 mL pipette for greater accuracy, they put 500.00 mL of tap water into the flask. They used warm water to help the sodium hydroxide dissolve readily. They then shook the flask, preventing the solution from coming out by putting their thumb over the end, until all the solid had dissolved.

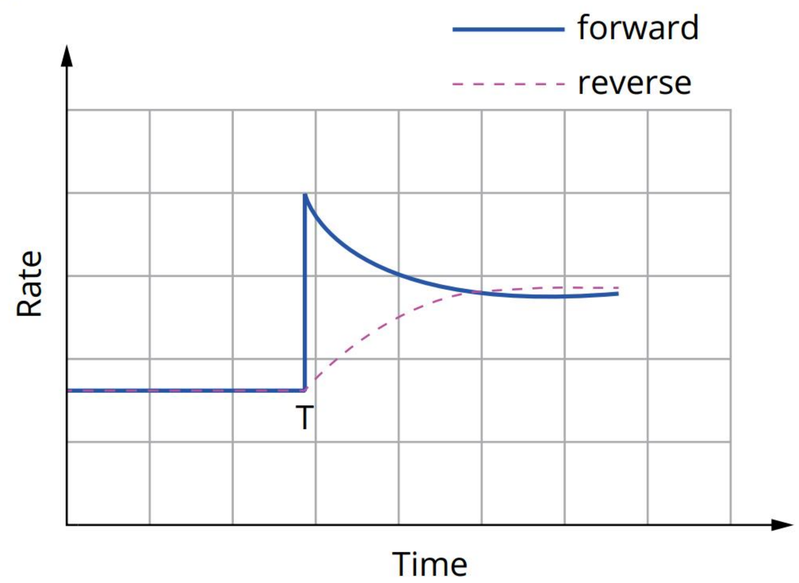
Identify five things the student did that would decrease the accuracy of the titration.

11 Consider the following readily reversible gas-phase reaction:



$$W(g) + 2X(g) \rightleftharpoons Y(g) + Z(g)$$

The graph below shows the changes to the rates of the forward and reverse reactions when some additional reactant, W, is added to an equilibrium mixture of these gases at time *T*.



a Explain how this graph shows that the mixture was at equilibrium before time *T*.

b Explain the changes in the rates of the forward and reverse reactions from time *T* using collision theory.

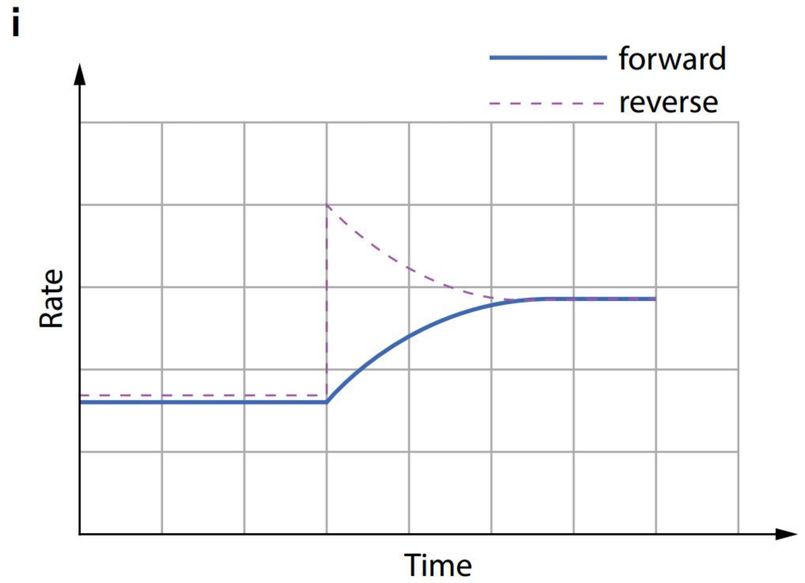
c The process was repeated several times, each time with a different change occurring at time *T*.

Changes tested included:

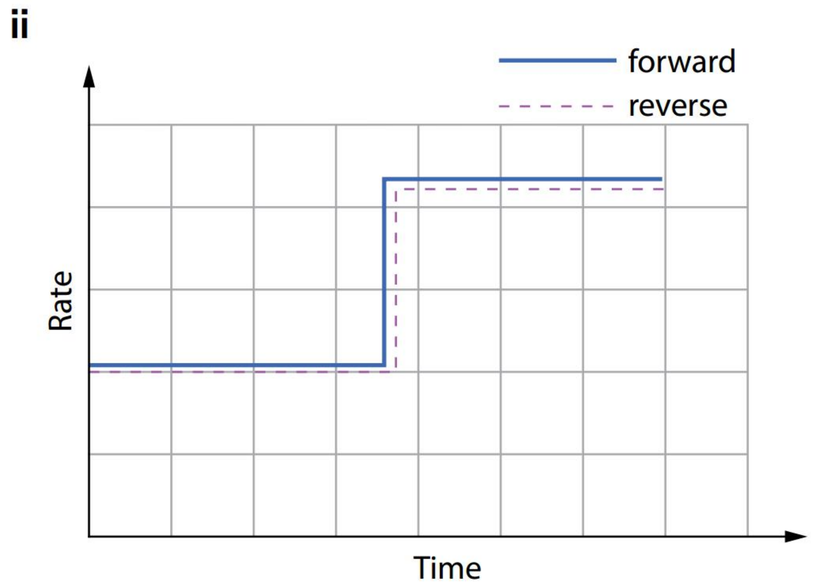
- removing W from the mixture
- removing Y
- adding Y
- adding an inert gas (argon)
- adding a catalyst
- increasing the volume of the container.

Select a change from this list that is consistent with the rate changes depicted in each of the graphs below. In each case, briefly justify your choice.

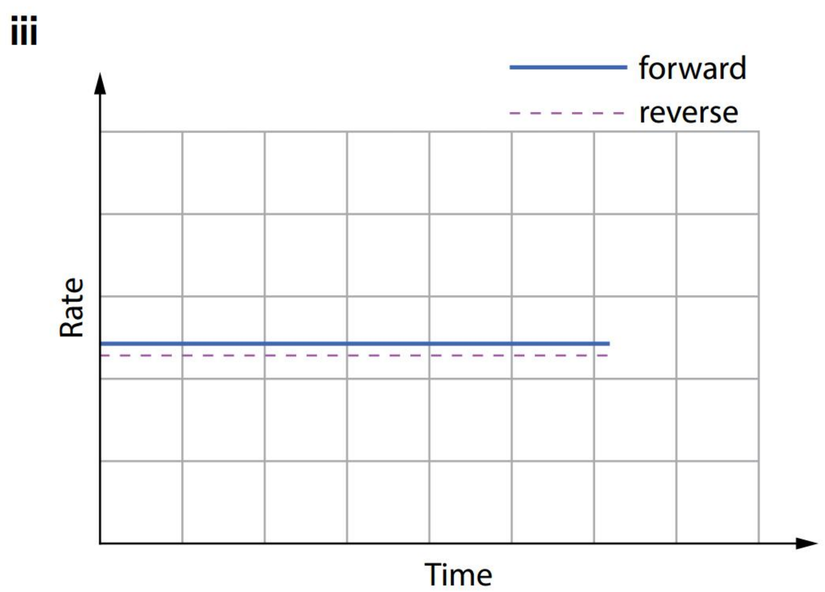
i



ii

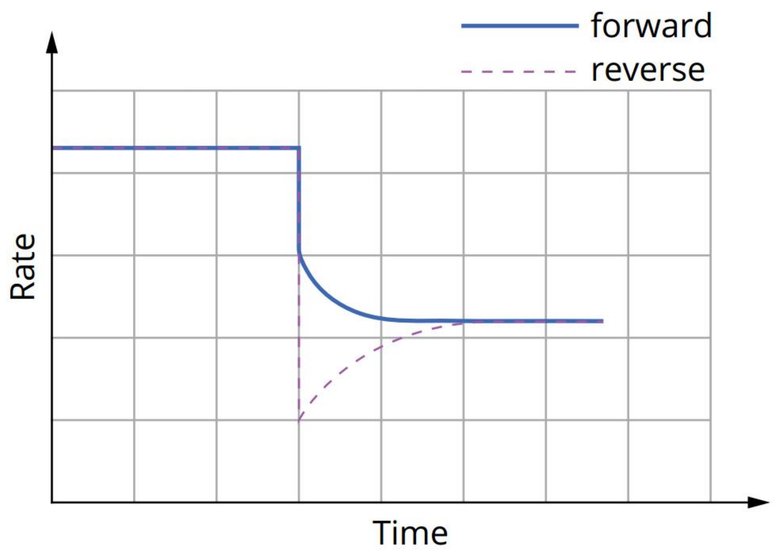


iii



*Use the following information to answer question parts **d**, **e** and **f**.*

The graph below shows the rate changes after lowering the temperature at time *T*.



d Explain why lowering the temperature causes an initial drop in both reaction rates.

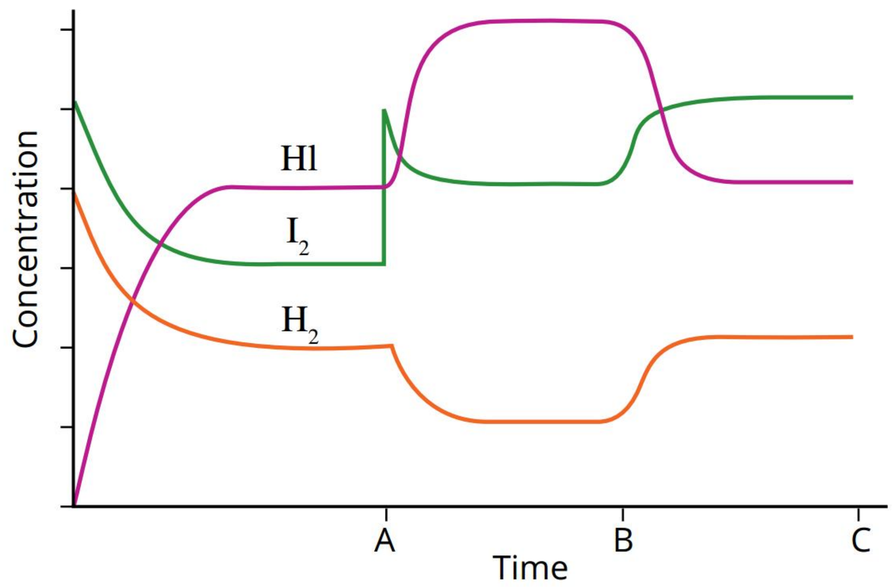
e Identify the direction of equilibrium favoured by the temperature decrease.

f Determine whether the reaction is exothermic or endothermic. Explain your reasoning.

12 The reaction between hydrogen and iodine in the gaseous phase to produce hydrogen iodide is described by the following equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H \text{ negative}$$

The following diagram shows the change in concentration of gaseous hydrogen, iodine and hydrogen iodide as the equilibrium is reached and disturbed.



a At point A, a sudden change has occurred to the system. Identify the change made at point A.

b At point B, another change has occurred. Identify a possible cause of this change.

c Show a point on the time axis of the graph where the system is at equilibrium.

d Modify the graph, extending it past point C, to show what would happen to the concentration of the gases if the volume of the reaction vessel was doubled. Assume the temperature remains constant. Draw the curve until equilibrium is re-established.

13 Methanol is used as a fuel for some racing cars. The synthesis of methanol from methane involves two reactions:

- the reaction of methane with steam to yield carbon monoxide and hydrogen
- an exothermic reaction between carbon monoxide and hydrogen to produce methanol.

a Represent the two reactions as equations.

b The reaction of carbon monoxide with hydrogen is performed at about 250°C and 104 kPa. Copper, zinc oxide and alumina are also present.

i Identify the likely function of the copper, zinc oxide and alumina in the reactor.

ii Predict how the yield would be affected if the reaction were performed at a higher temperature.

iii State two advantages of employing such a high pressure.

c Any process involving carbon monoxide presents hazards because of its toxicity, which arises because of its ability to bind strongly to haemoglobin in competition with oxygen.

$$Hb_4 + CO \rightleftharpoons Hb_4CO \quad K_{c1}$$
$$Hb_4 + O_2 \rightleftharpoons Hb_4O_2 \quad K_{c2}$$

K_{c1} is 20 000 times greater than K_{c2}.

i Referring to these competing equilibria, explain why exposure to carbon monoxide leads to decreased levels of oxyhaemoglobin (Hb_4O_2) in the blood.

ii Treatment for carbon monoxide poisoning often includes hyperbaric oxygen (pure oxygen at a pressure well above 100 kPa). Explain how this helps remove Hb_4CO from the blood.

14 An equilibrium is established when, in a closed system, gaseous phosphorus pentachloride (PCl_5) dissociates into gaseous phosphorus trichloride (PCl_3) and chlorine (Cl_2).

a Write a balanced equation for this equilibrium reaction.

b Determine the equilibrium law expression for this reaction.

c The following equilibrium concentrations exist at a particular temperature: $[PCl_5] = 0.5\,mol\,L^{-1}$, $[PCl_3] = 2.0\,mol\,L^{-1}$, $[Cl_2] = 1.6\,mol\,L^{-1}$. Calculate the value of the equilibrium constant at this temperature.

15 The concentration of hydrogen iodide gas in a sample at equilibrium is 9.30×10^{-4} M. It was formed by the combination of 5.00×10^{-4} moles of hydrogen gas and 1.00×10^{-3} moles of iodine vapour in a sealed 1.00 L vessel at 455.0°C. At equilibrium, all three gases are present.

The balanced equation for the reaction is:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Calculate the equilibrium constant, K_c, for the reaction at 455.0°C.

16 The K_a for hypobromous acid (HOBr) is 2.1×10^{-9}.

a Construct an equation for the dissociation of hypobromous acid in water.

b Given a 0.30 mol L^{-1} HOBr solution, calculate the:

i pK_a

ii pH

iii percentage dissociation.

c In calculating the pH and percentage dissociation, it can be assumed that the concentration of hypobromous acid at equilibrium is approximately the same as the initial concentration of hypobromous acid. Explain why this assumption is justified. Give reasons for your answer.

17 A commercial metal cleaning solution is known to contain nitric acid, HNO_3, as its active ingredient.

To determine the concentration of the cleaning agent, a 10.0 mL sample is diluted to 500 mL in a volumetric flask. 20.0 mL aliquots of this solution are then titrated against a 0.150 M solution of the weak base sodium carbonate, Na_2CO_3.

The burette readings obtained are shown in the table below.

Run	Initial volume (mL)	Final volume (mL)
1	50.00	32.45
2	30.00	10.10
3	50.00	32.50
4	32.00	14.55

a Write a balanced equation for the reaction occurring.

b Suggest a suitable indicator for this titration.

c Determine the dilution factor for the nitric acid.

d Determine the mean titre of the concordant titres.

e State two guidelines to follow when reading the burette.

f State what each of the following items of glassware should be rinsed with before the experiment:

i burette

ii volumetric flask

iii pipette.

18 Many household cleaners contain ammonia (NH_3) as the active ingredient. An acid–base titration with HCl is performed to determine the concentration of ammonia in a commercially available cleaner.

a The hydrochloric acid was standardised by titration against a 20.00 mL aliquot of a primary standard. The standard was prepared by dissolving 1.22 g of anhydrous sodium carbonate (Na_2CO_3) in a 250.0 mL volumetric flask that was filled to the calibration line with distilled water. The titration was carried out a number of times and the following titres were recorded: 20.01 mL, 19.40 mL, 19.39 mL, 18.92 mL and 19.38 mL.

i List the properties of anhydrous sodium carbonate that make it suitable for use as a primary standard.

ii Identify the volumes that should be used to calculate the average titre of hydrochloric acid.

iii Write a balanced equation for the reaction between hydrochloric acid and the solution of sodium carbonate.

iv Calculate the concentration of the standard sodium carbonate solution. The molar mass of Na_2CO_3 is 105.99 g mol^{-1}.

v Determine the concentration of the hydrochloric acid solution.

b Distilled water is used to dilute 10.00 mL of the cleaner to 100.0 mL in a volumetric flask. Next, 20.00 mL of this diluted cleaning solution is placed in a dry conical flask and titrated against the standardised hydrochloric acid solution from part **a** using methyl orange as an indicator. The average of three concordant titres is 17.40 mL.

i Write an equation for the reaction between ammonia and hydrochloric acid.

ii Calculate the concentration, in mol L^{-1}, of ammonia in the cleaner.

iii Calculate the mass, in g, of ammonia in a 750 mL bottle of cleaner.

iv Methyl orange is pink at a pH lower than 3.2 and yellow at a pH greater than 4.4.

Explain why methyl orange is a suitable indicator for this titration, and state the colour change that would be observed.

v Copy the table below and state whether each of the following changes to this titration procedure would lead to a result that is higher, lower or the same for the concentration of ammonia in the cleaner. Give an explanation for each answer.

	Result would be higher/lower/the same as the actual concentration of ammonia	Explanation
20.00 mL of water was added to the 20.00 mL of diluted cleaner solution in the conical flask prior to titration.		
Phenolphthalein indicator was used instead of methyl orange. Phenolphthalein is colourless at a pH less than 8.3 and pink at a pH higher than 9.5.		
The conical flask was washed, then rinsed with the diluted cleaner solution before using it.		

19 Chlorophenol red is an acid–base indicator that is yellow in acidic conditions and red in alkaline conditions. The indicator changes colour over the range of 5.4–6.8.

Test tube A contains 1.0 M HCl, and test tube B contains 1.0 M NaOH. A few drops of chlorophenol red are added to both test tubes.

a Using the symbols of HCR for chlorophenol red, write an equation for the reaction between chlorophenol red and water. Indicate under your equation which species is yellow and which is red.

b Identify the colour of chlorophenol red in test tube A and explain why this colour forms.

c Identify the colour of chlorophenol red in test tube B and explain why this colour forms.

d Assuming the transition point is at the midway point of the pH transition range provided, calculate the K_a value of chlorophenol red.

20 Phenol red is an acid–base indicator. The protonated form of the indicator, represented for simplicity by HPhr, is yellow, whereas the deprotonated form, Phr^-, is red. Phenol red has a pK_a value of 7.9.

a i Construct a chemical equation showing the relationship between the protonated and deprotonated forms of phenol red.

ii Deduce the equilibrium law expression for this reaction.

b i Identify the pH at the end point of a titration using phenol red as the indicator.

ii Propose a pH range over which phenol red would be expected to change colour.

iii Explain for which type of acid–base titration phenol red would be a suitable indicator.

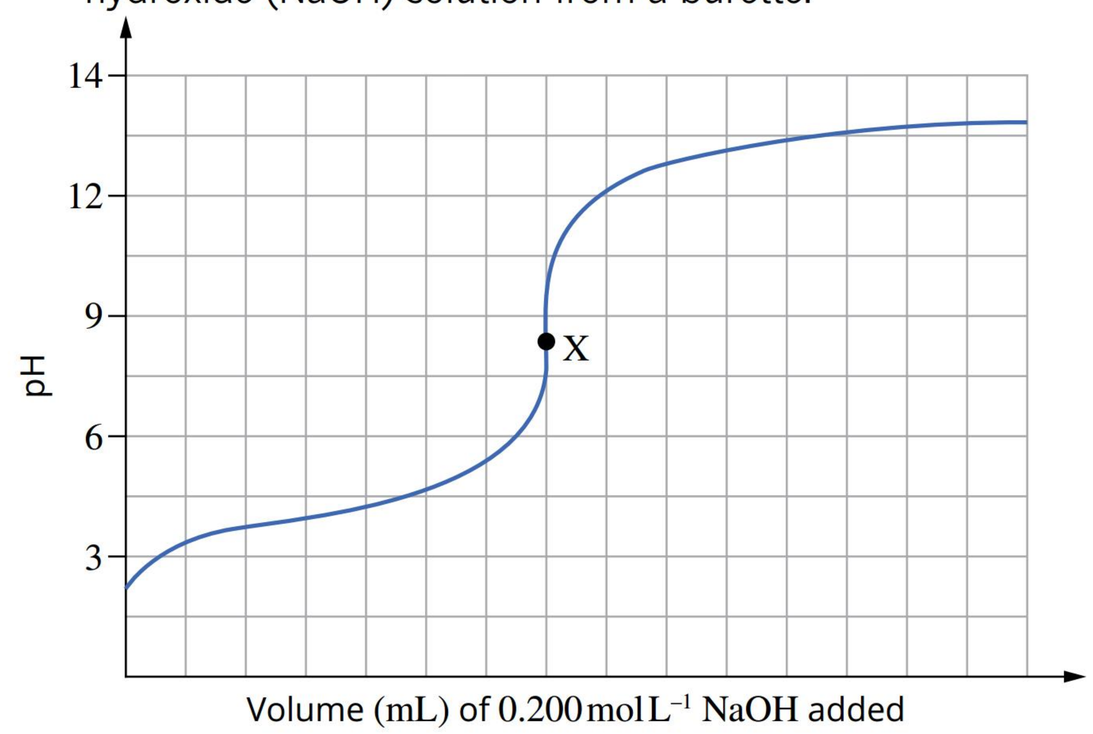
c Copy the table below and use your understanding of indicator chemistry to predict the colour of the indicator at the listed pH values. Justify your predictions.

pH	Phenol red colour	Justification
1.0		
7.0		
7.9		
8.4		
13.0		

21 Benzoic acid is a weak acid used as a preservative, for example, in soft drinks. In aqueous solution, it dissociates according to the equation:

$$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$$

The graph shows the changes in pH that occur when 20.00 mL of 0.100 mol L^{-1} benzoic acid solution in a conical flask is titrated with 0.200 mol L^{-1} sodium hydroxide (NaOH) solution from a burette.



a Explain the significance of point X.

b Determine the volume of sodium hydroxide that has been added to the conical flask at point X.

c The pH range for the colour change is 3.0 (yellow) to 4.6 (blue) for the indicator bromophenol blue. Predict whether bromophenol blue would be a suitable indicator for determining the equivalence point of a titration of benzoic acid with sodium hydroxide. Explain your answer.

d The reaction of benzoic acid with the base, sodium hydroxide, is often referred to as a neutralisation reaction. Explain why the pH of point X is not 7.

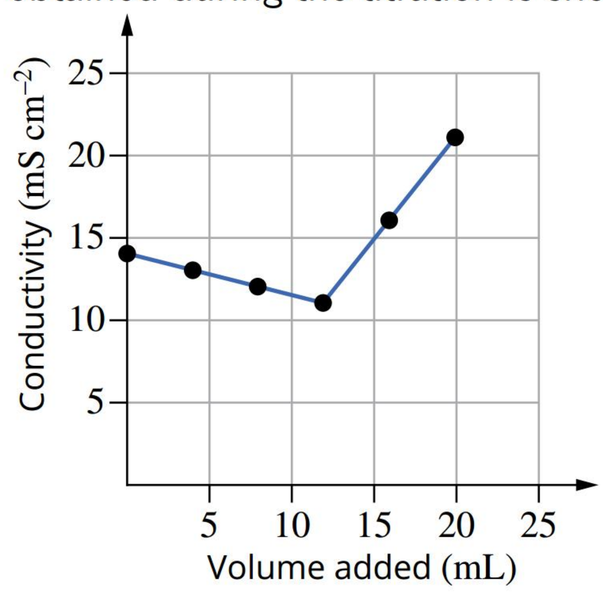
e Show the equivalence point, buffer region and the point where pK_a = pH on the graph.

f Determine the pK_a value of benzoic acid from the graph.

g Explain why the addition of a small volume of sodium hydroxide solution to the conical flask, in the buffer region, only causes a small change in pH.

h Describe the change in pH if a small amount of acid is added to a solution of a benzoic acid/benzoate buffer.

22 A solution containing barium ions is added to a burette. A 20.00 mL aliquot of 0.14 mol L^{-1} sulfuric acid solution is added to the beaker under the burette. Electrodes are placed in the solution to allow the conductivity of the beaker contents to be recorded. The conductivity graph obtained during the titration is shown below.



a Write an ionic equation for the reaction occurring in the beaker (a precipitate forms).

b Explain why the conductivity drops initially.

c Explain why the conductivity increases after the equivalence point.

d Calculate the concentration of the barium ions in the original solution.

23 Lead(II) carbonate is considered insoluble in water.

a Calculate the value of K_{sp} at 25°C if the molar solubility is 3.80×10^{-7} mol L^{-1}.

b Predict whether a precipitate will form when 0.0002 g of lead carbonate is added to 500 mL of water at 25°C.

Topic 2: Oxidation and reduction

Multiple choice

1 Identify the option in which the nitrogen atoms are arranged in order of increasing oxidation number.

A NH_4^+, N_2, NO, NO_3^-

B NO_3^-, NO, NH_3^+, N_2

C NO_2, N_2, NO, HNO_3

D NO_3^-, NO, N_2, NH_3

2 Identify the option that is not a redox reaction.

A $2Mg(s) + O_2(g) \rightleftharpoons 2MgO(s)$

B $2H_2O_2(aq) \rightleftharpoons 2H_2O(l) + O_2(g)$

C $Pb^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons PbCl_2(s)$

D $Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$

3 An alkaline solution was electrolysed, producing hydrogen and oxygen. Which half-equation shows the reaction at the anode?

A	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
B	$4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$
C	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
D	$2OH^-(aq) + 2e^- \rightarrow \frac{1}{2}O_2(g) + H_2O(l)$

4 Select the statement that is true for the reaction:

$H_2O_2(aq) + 2H^+(aq) + 2Cl^-(aq) \rightleftharpoons 2H_2O(l) + Cl_2(g)$

A Hydrogen peroxide is reduced and the hydrogen ion is oxidised.

B The chloride ion is oxidised and the oxygen in hydrogen peroxide is reduced.

C Hydrogen peroxide is the reducing agent and the hydrogen ion is the oxidising agent.

D The oxidising agent is the chloride ion and the reducing agent is hydrogen peroxide.

5 Identify the equation involving antimony (Sb) that is a redox reaction.

A $SbF_5 + KF \rightleftharpoons KSbF_6$

B $2SbCl_3 + 3H_2O \rightleftharpoons Sb_2O_3 + 6HCl$

C $2Sb + 3Zn + 6HCl \rightleftharpoons 2SbH_3 + 3ZnCl_2$

D $Sb_2(SO_4)_3 + 3H_2S \rightleftharpoons Sb_2S_3 + 3H_2SO_4$

6 Select the option that best describes the features of an anode in a galvanic cell.

	Polarity	Electrode reaction
A	positive	oxidation
B	positive	reduction
C	negative	oxidation
D	negative	reduction

7 Select the option that is correct for both galvanic and electrolytic cells.

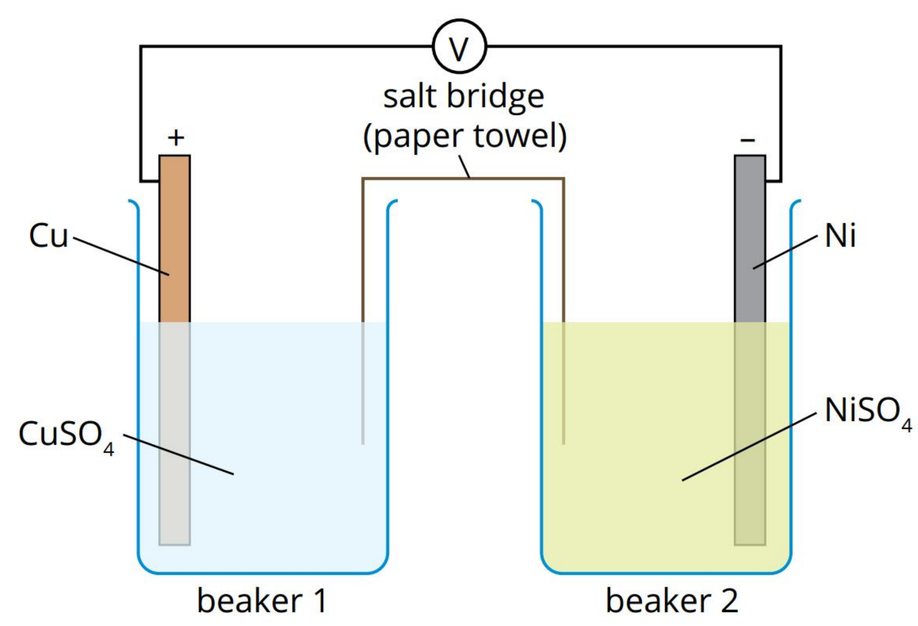
A Chemical energy is converted into electrical energy.

B Electrons flow from the anode to the cathode.

C A salt bridge is required to separate reactants.

D Reduction occurs at the positive electrode.

8 An electrochemical cell was made by dipping a copper rod into a solution of 1.0 mol L^{-1} $CuSO_4$ in one beaker and dipping a nickel rod into a solution of 1.0 mol L^{-1} $NiSO_4$ in another beaker. The metals were connected with wire, and the two solutions were connected by a piece of paper towel that had been soaked in a potassium nitrate solution. The cell is shown in the following diagram.



The solution in beaker 1 was initially coloured blue, owing to the presence of Cu^{2+} ions. The solution in beaker 2 was initially coloured green because of the presence of Ni^{2+} ions. Predict which of the following changes might be possible to detect after the galvanic cell has been discharging for a period of time.

A The blue colour in beaker 1 has faded and the mass of the nickel electrode has increased.
B The blue colour in beaker 1 has faded and the mass of the nickel electrode has decreased.
C The green colour in beaker 2 has faded and the mass of the copper electrode has increased.
D The green colour in beaker 2 has faded and the mass of the copper electrode has decreased.

9 Using the electrochemical series (Table 2 in Appendix E), determine which one of the following reactions would not be spontaneous.

A $2I^-(aq) + Pb^{2+}(aq) \rightleftharpoons I_2(s) + Pb(s)$
B $2Ag^+(aq) + Ni(s) \rightleftharpoons 2Ag(s) + Ni^{2+}(aq)$
C $2H^+(aq) + Fe(s) \rightleftharpoons Fe^{2+}(aq) + H_2(g)$
D $Br_2(aq) + 2Fe^{2+}(aq) \rightleftharpoons 2Br^-(aq) + 2Fe^{3+}(aq)$

10 Hydrogen gas (H_2) is bubbled through a solution of $Sn^{4+}(aq)$. Predict which one of the following observations is most likely.

A No reaction will occur.
B A precipitate of SnH_4 will form.
C The pH of the solution will decrease.
D Oxygen gas will form from the dissociation of water.

11 The following equations involve ions of the transition metal vanadium. The half-cell potential $E°$ (V) is shown for each equation.

$$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq) \qquad E° = -0.25\,V$$
$$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l) \qquad E° = +0.36\,V$$
$$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l) \qquad E° = +1.00\,V$$

Identify the option that gives the strongest oxidising and reducing agents.

	Oxidising agent	Reducing agent
A	VO_2^+	V^{2+}
B	VO_2^+	VO^{2+}
C	V^{3+}	VO^{2+}
D	V^{2+}	VO_2^+

12 A ring is to be covered with a thin layer of gold by electroplating from a solution of Au^{3+}. Identify the terminal of the power supply to which the ring should be attached and name this terminal.

A positive terminal; anode
B negative terminal; anode
C positive terminal; cathode
D negative terminal; cathode

13 Which of the following pairs of electrolytic cells will produce the same products at the electrodes? (Inert electrodes are used.)

A NaCl(l) and 0.1 M NaCl(aq)
B KBr(l) and 0.1 M KBr(aq)
C $CuCl_2$(l) and 0.1 M $CuCl_2$(aq)
D $CuBr_2$(l) and 0.1 M $CuBr_2$(aq)

14 The volume of chlorine gas produced in an electrolytic cell at STP is measured as 4.54 L.

The cell was running for 100 minutes. The current used was, in amps:

A 3.22
B 4.66
C 6.43
D 12.9

15 A current of 9.65 A is passed through a cell for 1000 seconds. 0.050 mole of metal is deposited on the negative electrode in this time. The electrolyte used could be a solution of:

A $AgNO_3$
B $Cu(NO_3)_2$
C $Al(NO_3)_3$
D $Mg(NO_3)_2$

16 Select the alternative that correctly indicates the polarity of the anode in a galvanic cell and an electrolytic cell.

	Polarity of the anode in a galvanic cell	Polarity of the anode in an electrolytic cell
A	positive	negative
B	negative	positive
C	positive	positive
D	negative	negative

Short answer

1 For each of the reactions represented below:

- identify them as redox or non-redox reactions
- list the changes in oxidation state for each redox reaction
- identify the oxidising agent and the reducing agent for each redox reaction.

a $HIO_3(aq) + 3SO_2(g) \rightleftharpoons 3SO_3(aq) + HI(aq)$
b $SO_3(g) + Ca(OH)_2(aq) \rightleftharpoons CaSO_4(s) + H_2O(l)$
c $4Fe(OH)_2(s) + 2H_2O(l) + O_2(g) \rightleftharpoons 4Fe(OH)_3(aq)$
d $NaH(s) + H_2O(l) \rightleftharpoons H_2(g) + NaOH(aq)$
e $2C_2H_6(g) + 7O_2(g) \rightleftharpoons 4CO_2(g) + 6H_2O(l)$

2 Balance each of the following unbalanced redox reactions. Identify the oxidising agent and the reducing agent.

a $Al(s) + Br_2(aq) \rightleftharpoons Al^{3+}(aq) + Br^-(aq)$
b $ClO^-(aq) + S_2O_3^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + Cl^-(aq)$
c $H_2O_2(aq) + MnO_4^-(aq) \rightleftharpoons O_2(aq) + MnO_2(s)$
d $U^{4+}(aq) + MnO_4^-(aq) + H_2O(l) \rightleftharpoons Mn^{2+}(aq) + UO_2^+(aq) + H^+(aq)$

3 For the following reactions, use the standard electrode potentials provided to construct the:

- oxidation half-equation
- reduction half-equation
- overall ionic equation.

Conjugate redox pair (oxidising agent/reducing agent)	$E°$ (V)
$Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$	1.36
$Fe^{3+}(aq)/Fe^{2+}(aq)$	0.77
$I_2(s)/I^-(aq)$	0.54
$S(s)/H_2S(g)$	0.17

a A solution of sodium iodide is added to an acidified solution of potassium dichromate.

b Hydrogen sulfide gas is bubbled into a solution of iron(III) chloride.

c Predict, using the information provided in the table above, the identity of the two half-cells that, when used in a galvanic cell, will generate the greatest cell potential at standard conditions. Calculate the cell potential difference generated by this cell.

d Discuss the limitations of predictions based on standard electrode potentials.

4 Explain each of the following statements.

a A piece of iron metal that is partly exposed to a moist atmosphere and partly buried in the ground corrodes much more rapidly beneath the surface of the ground.

b It is unwise to use a copper nut on a steel bolt in an exposed environment.

5 A useful electrochemical cell for small devices, such as watches and phones, makes use of silver oxide and zinc as described by the equation:

$Zn(s) + Ag_2O(s) + H_2O(l) \rightleftharpoons 2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq)$

The cell potential is 1.50 V.

a Identify the anode and cathode, and state the polarity of each electrode.

b Show the half-equations for the reactions occurring at both the anode and the cathode.

c Name the oxidising agent and the reducing agent in the cell.

d Determine the standard reduction potential for the half-cell containing $Ag_2O(s)$.

6 For each of the following reactions:

i Calculate the oxidation numbers for all species in the equation.

ii Identify the reaction as redox or non-redox.

iii If the reaction is a redox reaction, identify the oxidising agent and the reducing agent, giving reasons for your answers.

a $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

b $4Fe(OH)_2(s) + 2H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(aq)$

c $HNO_3(aq) + LiOH(aq) \rightarrow LiNO_3(aq) + H_2O(l)$

d $H_2O_2(aq) + PbO_2(s) + 2H+(aq) \rightarrow O_2(g) + Pb_2+(aq) + 2H_2O(l)$

7 For each of the following unbalanced redox reactions (all occurring in acidic aqueous solution):

i Identify the reactant that is oxidised and the reactant that is reduced.

ii Write the balanced half-equations for the oxidation and reduction reactions.

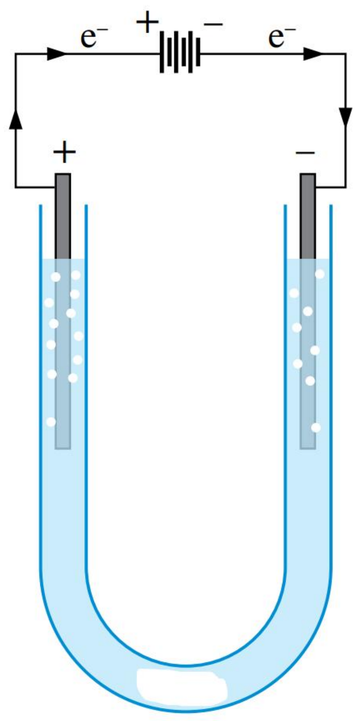
iii Write the balanced overall ionic equation for the reaction.

a $Al(s) + HOCl(aq) \rightarrow Al^{3+}(aq) + Cl_2(g)$

b $Ag(s) + BrO_3^-(aq) \rightarrow Ag^+(aq) + Br^-(aq)$

c $Cr_2O_7^{2-}(aq) + H_2SO_3(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$

8 A series of electrolyses is carried out under standard conditions in a U-tube, as shown in the following diagram.



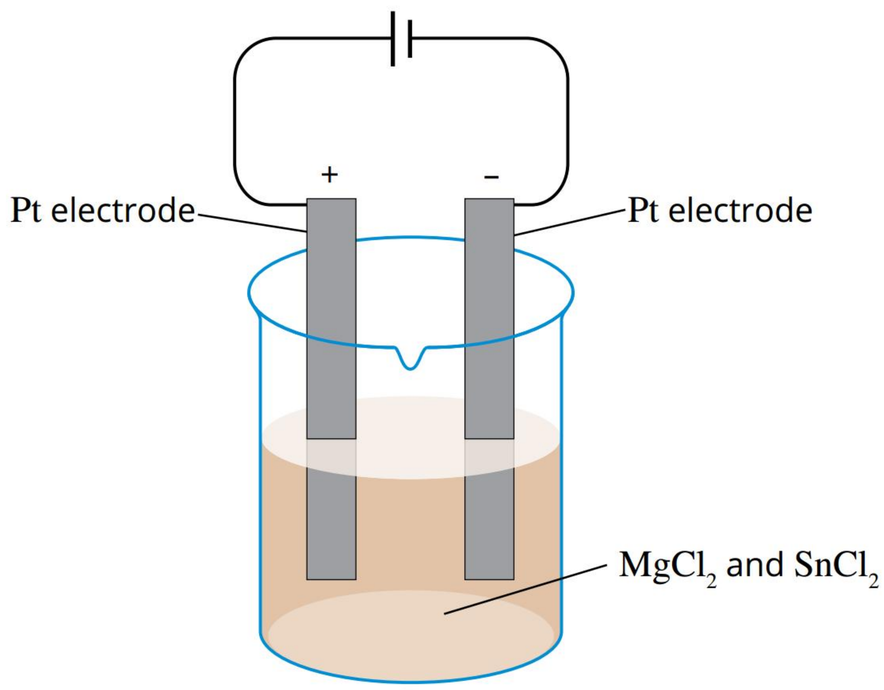
The electrolyte solution in each case and the electrode materials used are listed below.

Solution	Electrode materials	
	Positive electrode	Negative electrode
$KI(aq)$	carbon	carbon
$PbCl_2(aq)$	carbon	carbon
$AlCl_3(aq)$	copper	copper
Na_2SO_4	platinum	platinum

a Show half-equations for the reactions predicted to occur at the positive and negative electrodes.

b State one visible change you would observe to confirm the formation of your predicted products.

9 A 100 mL solution containing a mixture of magnesium chloride and tin(II) chloride is prepared by dissolving 0.025 mol of each in water. Platinum electrodes are placed in the solution and a small current is passed through it, as shown in the diagram below.



a Using the standard electrode potentials (Table 2 in Appendix E), show half-equations for the electrode reactions occurring just after electrolysis is started at the:
  i anode
  ii cathode.

b After electrolysis has been occurring for a considerable period of time, the metal ions required for the reaction at the cathode will have been used up, and a new electrode reaction will occur at the cathode. Show a half-equation for the next electrode reaction that occurs at the cathode.

c Identify the major difference that would occur in the cell if the solution that was used had been a saturated solution of tin(II) chloride.

10 Compare and explain the anode and cathode reactions that occur when a direct electric current is passed through:

a molten sodium chloride

b a 0.10 mol L^{-1} solution of sodium chloride

c a concentrated solution of sodium chloride.

Assume that inert electrodes are used in each of the electrolyses.

11 Carbon electrodes are connected to a power supply and placed in a solution of zinc nitrate. A current of 3.60 A is passed through the cell for 1.00 hour. Calculate the mass change of the cathode during the experiment.

12 Discuss briefly, using sodium and sulfur as examples, how the ability of elements to act as an oxidising or reducing agent can be predicted from their position in the periodic table.

13 This question requires you to compare galvanic cells with electrolytic cells.

a List two structural features (components) that both types of cells possess.

b Compare the energy transformations occurring in a galvanic cell with those occurring in an electrolytic cell.

c Explain why the negative electrode of a galvanic cell is the site of oxidation, whereas the negative electrode of an electrolytic cell is the site of reduction.

d Explain why a galvanic cell is always constructed to keep its reacting oxidising and reducing agents apart, whereas in an electrolytic cell, they are usually combined in the same electrolyte mixture, and instead, steps are taken to keep the cell products apart.

14 In a commercially available dry cell, a voltage of about 1.48 V is produced by an electron transfer reaction between MnO_2 and Zn. In this reaction, $MnO_2(s)$ is converted to $Mn_2O_3(s)$.

a State the names of MnO_2 and Mn_2O_3.

b Show the half-equations for the oxidation and reduction reactions in the dry cell.

c Calculate the reduction potential for the reduction reaction of MnO_2, assuming standard conditions.

d Suggest why the paste in the dry cell becomes less acidic as the cell operates.

e Explain why the dry cell described above is called a primary cell.

15 A half-cell is made by placing a copper electrode in a solution containing Cu^{2+} ions, and another is made by placing a graphite electrode in an aqueous solution of iodide ions and iodine (a brown colour in aqueous solution). The two half-cells are connected correctly.

a State what would need to be done to 'correctly connect' the two half-cells.

b Show two balanced half-equations for the reactions that occur at the electrodes. Write the net ionic equation for the cell.

c **i** State the direction of electron flow.
  ii State the direction of flow of the anions in the salt bridge.
  iii Identify the cathode and the anode.
  iv Calculate the cell potential for the cell (assume standard conditions).
  v Explain the purpose of the graphite electrode and determine whether any other solid material, such as Pb or Fe, could be used instead in this half-cell. Explain your answer.
  vi Predict what you would observe to happen in each half-cell over a period of time.

16 The standard electrode potentials for some conjugate redox pairs are given in the following table.

Conjugate redox pair (oxidising agent/ reducing agent)	E° (V)
$O_2(g)/H_2O(l)$	1.23
$H_2O_2(aq)/H_2O(l)$	1.78
$O_2(g)/H_2O_2(aq)$	0.70
$Fe^{3+}(aq)/Fe^{2+}(aq)$	0.77
$Na^+(aq)/Na(s)$	2.71
$SO_4^{2+}(aq)/SO_2(g)$	0.16
$CO_2(g)/ C_2O_4^{2-}$	0.49
$MnO_4^-(aq)/Mn^{2+}(aq)$ (purple colourless)	1.49

a Briefly describe how an acidified solution of potassium permanganate can be used to distinguish between:

i water and hydrogen peroxide

ii iron(II) nitrate solution and iron(III) nitrate solution

iii sodium oxalate and sodium sulfate solution.

(Hint: The data in the table should be helpful with this question.)

b Predict any observations you would expect to make when potassium permanganate is added to the solutions listed in part **a**. Justify your predictions in terms of the principles of redox chemistry you have studied in this course. Refer to the information provided in the table. Use chemical equations where appropriate.

17 A student was asked to write a balanced overall ionic equation for each of the following reactions. The descriptions of the reactions and the ionic equations written by the student are given below.

For each reaction:

i Analyse the student's equation by writing the oxidation numbers for all the species above them in the equation.

ii Evaluate the student's equation by comparing it to the description of the reaction and listing any mistakes the student has made.

iii Write the correct balanced overall ionic equation for the reaction.

a Some iron filings (Fe(s)) were added to a solution of sodium bromate ($NaBrO_3(aq)$) in acidic solution. The iron dissolved to make $Fe^{2+}(aq)$, and bromide ions ($Br^-(aq)$) were also made.

Student's ionic equation: $5Fe(s) + 2BrO_3^-(aq) + 12H^+(aq) \rightarrow Br_2(aq) + 5Fe^{2+}(aq) + 3H_2O(l)$

b An acidified aqueous solution of potassium chlorate(VII) ($KClO_4(aq)$) was mixed with an aqueous solution of potassium iodide ($KI(aq)$). The mixture turned yellow and the products were chloride ions ($Cl^-(aq)$) and iodine ($I_2(s)$).

Student's ionic equation: $ClO_4^-(aq) + I_2(aq) + 4H_2O(l) \rightarrow Cl^-(aq) + 2I^-(aq) + 8H^+(aq)$

18 Which of the following electrolytic solutions, $MgCl^2$, KI and $CuBr^2$, will only produce hydrogen and oxygen?

19 **a** Write the half-cell reactions that take place at the anode and cathode in the electrolysis of molten calcium chloride using inert electrodes.

b Calculate the minimum voltage that is required for this process.

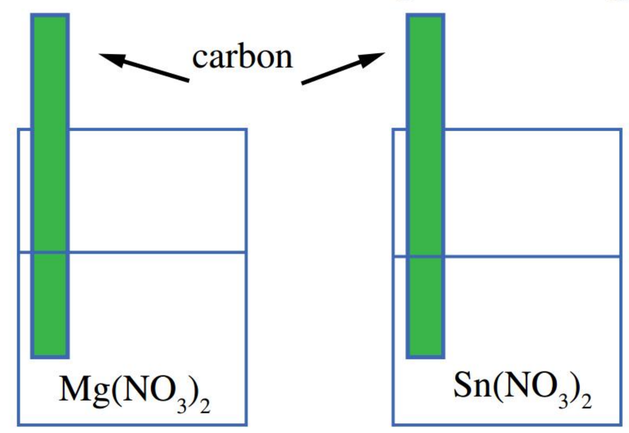
20 Sodium and chlorine are produced by electrolysis of molten sodium chloride in the Downs cell. A typical Downs cell runs at 600°C, 8 V and with a current of 35.0 kA.

a In a 24-hour period, what mass of sodium metal, in kg, will be produced?

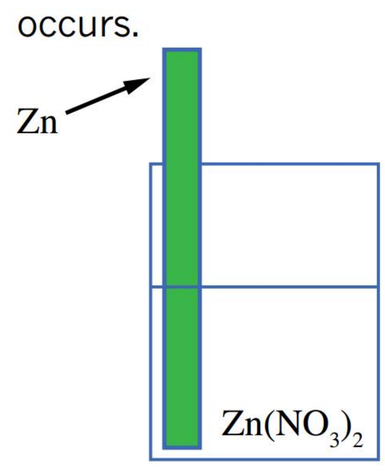
b In a 24-hour period, what volume of chlorine gas, measured under STP, will be produced?

21 Half-cells of magnesium nitrate and tin(II) nitrate are prepared with carbon electrodes.

a Which ion is the strongest oxidising agent?



b Each of the half-cells is connected in turn to a zinc half-cell. One of the combinations will not produce a voltage. Identify which of the combinations will not produce a voltage and explain why no reaction occurs.



c Determine the cell potential for the combination that does react.

22 A student designed an experiment to determine the order of the following four reduction reactions in the electrochemical series.

$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$

The student prepared half-cells for each reaction. The concentration of reactants in each half-cell was kept constant. Different sets of half-cells were combined in pairs to make a series of galvanic cells. A fresh salt bridge containing a solution of potassium nitrate was used in each galvanic cell. A voltmeter was used to measure the potential difference (voltage) produced by each galvanic cell. The direction of the deflection of the needle of the voltmeter was used to determine the polarity of the half-cell.

The student's results are summarised in the following table.

Half-cell pair	Positive half-cell	Potential difference (V)
$Pb^{2+}(aq)/Pb(s)$ and $Mg^{2+}(aq)/Mg(s)$	$Pb^{2+}(aq)/Pb(s)$	2.25
$Pb^{2+}(aq)/Pb(s)$ and $Cu^{2+}(aq)/Cu(s)$	$Cu^{2+}(aq)/Cu(s)$	0.46
$Pb^{2+}(aq)/Pb(s)$ and $Ag^+(aq)/Ag(s)$	$Ag^+(aq)/Ag(s)$	0.96
$Mg^{2+}(aq)/Mg(s)$ and $Cu^{2+}(aq)/Cu(s)$	$Cu^{2+}(aq)/Cu(s)$	2.71
$Mg^{2+}(aq)/Mg(s)$ and $Ag^+(aq)/Ag(s)$	$Ag^+(aq)/Ag(s)$	3.21
$Cu^{2+}(aq)/Cu(s)$and $Ag^+(aq)/Ag(s)$	$Ag^+(aq)/Ag(s)$	0.50

a Sort the reduction reactions in order from strongest oxidising agent to weakest oxidising agent using the results provided. Explain how you used the experimental evidence to determine the order of the relative strength of the oxidising agents.

b i Determine the potential difference provided by each half-cell if the potential provided by the $Cu^{2+}(aq)/Cu(s)$ half-cell is 0.36 V.

ii Sort the reduction equations into an electrochemical series.

iii Explain why these half-cell potentials do not match those provided in a table of standard electrode potentials.

c Draw a fully labelled diagram showing the galvanic cell produced by the combination of the $Mg^{2+}(aq)/Mg(s)$ and $Ag^+(aq)/Ag(s)$ half-cells.

d Explain the function of the salt bridge in a galvanic cell and why a fresh salt bridge is used in each galvanic cell.

e i Another way of determining the relative reactivity of metals and ions is to add a metal to a solution of metal ions. Copy and complete the following table by indicating if a metal/metal ion displacement reaction is expected to occur when the combinations of metal and metal ions are mixed.

	Metal ions			
Metal	$Pb^{2+}(aq)$	$Mg^{2+}(aq)$	$Cu^{2+}(aq)$	$Ag^+(aq)$
Pb				
Mg				
Cu				
Ag				

ii Show balanced equations for each reaction that occurs.

f Compare the energy changes that occur in a galvanic cell with the energy changes that occur when the oxidising and reducing agents are in direct contact.

23 Use the electrochemical series (Table 2 in Appendix E) to design a galvanic cell with an overall cell potential of approximately $E^\circ = 2.00$ V.

a Draw a labelled diagram of the cell showing the movement of electrons and negative ions.

b Write the balanced half-equation for the anode reaction.

c Write the balanced half-equation for the cathode reaction.

d Write the overall reaction in the cell and the overall cell potential.

e Suggest a suitable electrolyte for the salt bridge.

24 A power supply is connected in series to two electrolytic cells. The first cell contains molten silver chloride, and the second contains molten aluminium oxide (Al_2O_3). Inert electrodes are used, and the current is held constant the whole time.

The mass of the cathode in the silver cell is monitored continuously. After 8.00 minutes, the mass of the electrode has increased from 45.862 g to 46.654 g.

a Predict the likely mass change at the cathode after the cell has been running for 10.0 minutes.

b Determine the mass change of the cathode in the aluminium cell in the first 8.00 minutes.

c Refer to the data presented in this question to:

i state and explain Faraday's first law

ii state and explain Faraday's second law.

25 A current of 2.80 A is passed through a dilute solution of copper(II) chloride for 45.0 minutes. Inert electrodes are used, and the gas produced is collected and stored at STP.

a Calculate the mass of copper deposited.

b Calculate the volume of gas collected.

26 Electrolytic cells are used in industry to extract metals such as aluminium from their ore, as well as to refine metals such as copper. Electrolysis is used to purify copper. A particular sample of copper contains 1% impurities. These impurities consist of silver, gold, zinc and lead.

Explain how impure copper can be purified by electrolysis. Include in your answer:

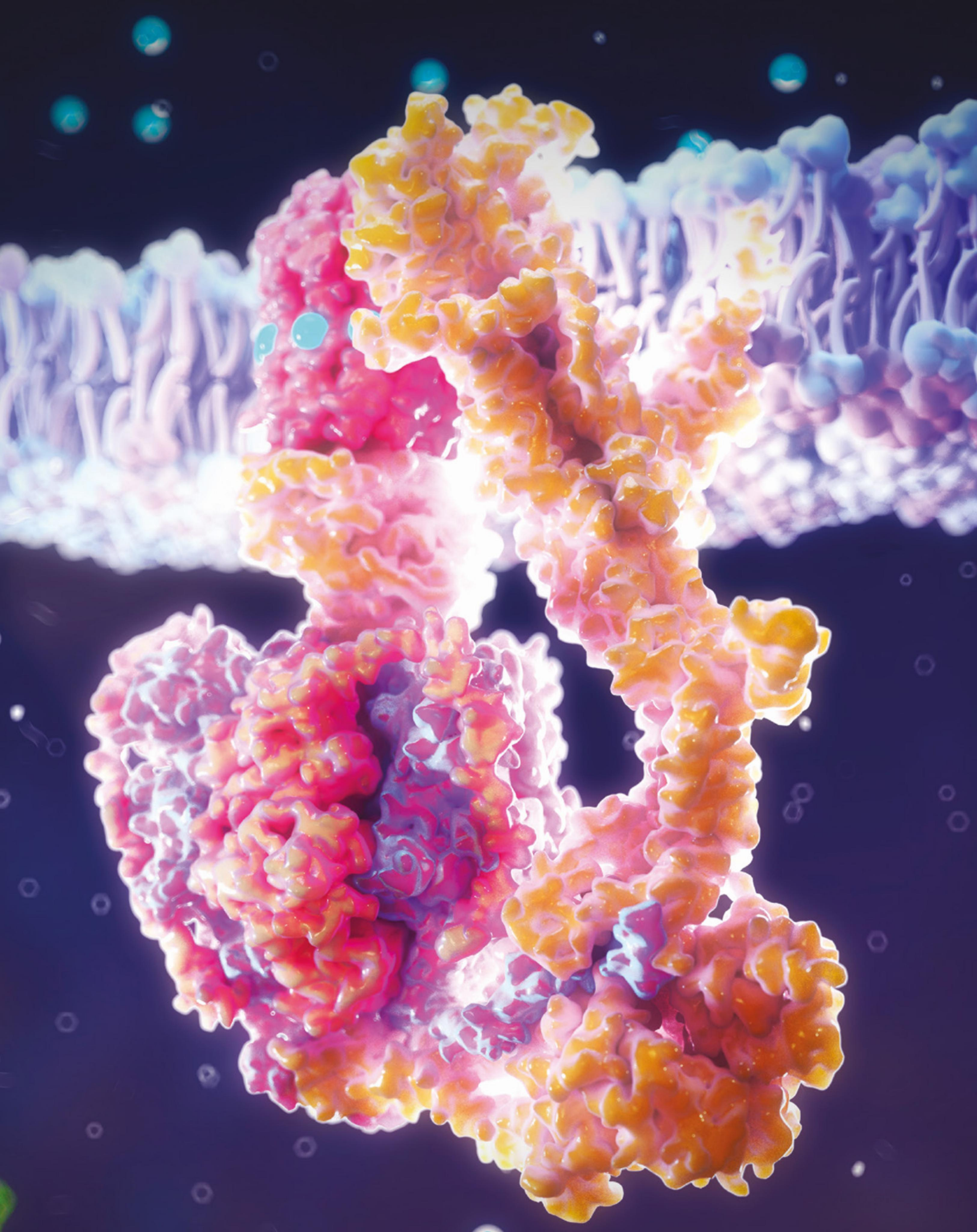
- half-equations for any reaction that occurs
- a labelled diagram showing the essential features of the electrolytic cell
- a description of what happens to the metal impurities as the electrolysis proceeds.

27 A cell was set up, and a 5.0 A current was passed through the platinum electrodes for 10 minutes. When the power supply was switched off, the mass of the cathode had increased by 0.54 g.

The chemist knew that the electrolyte was one of the following solutions: $AgNO_3$, $Cd(NO_3)_2$, $Pb(NO_3)_2$ and $Cr(NO_3)_3$.

Which solution was used in the cell?

28 A dilute solution of sodium chloride is electrolysed using inert electrodes. Explain what would happen to the colour of the solution around the positive and negative electrodes when a couple of drops of phenol red were added at each electrode. Use half-cell reactions to support your explanation.



UNIT 4 Structure, synthesis and design

TOPIC 1 Properties and structure of organic materials

TOPIC 2 Chemical synthesis and design

Unit 4 objectives

Students will:

- describe and explain the properties and structure of organic materials and chemical synthesis and design
- apply understanding of the properties and structure of organic materials and chemical synthesis and design
- analyse evidence about the properties and structure of organic materials and chemical synthesis and design
- interpret evidence about the properties and structure of organic materials and chemical synthesis and design
- investigate phenomena associated with the properties and structure of organic materials and chemical synthesis and design
- evaluate processes, claims and conclusions about the properties and structure of organic materials and chemical synthesis and design
- communicate understandings, findings, arguments and conclusions about the properties and structure of organic materials and chemical synthesis and design.

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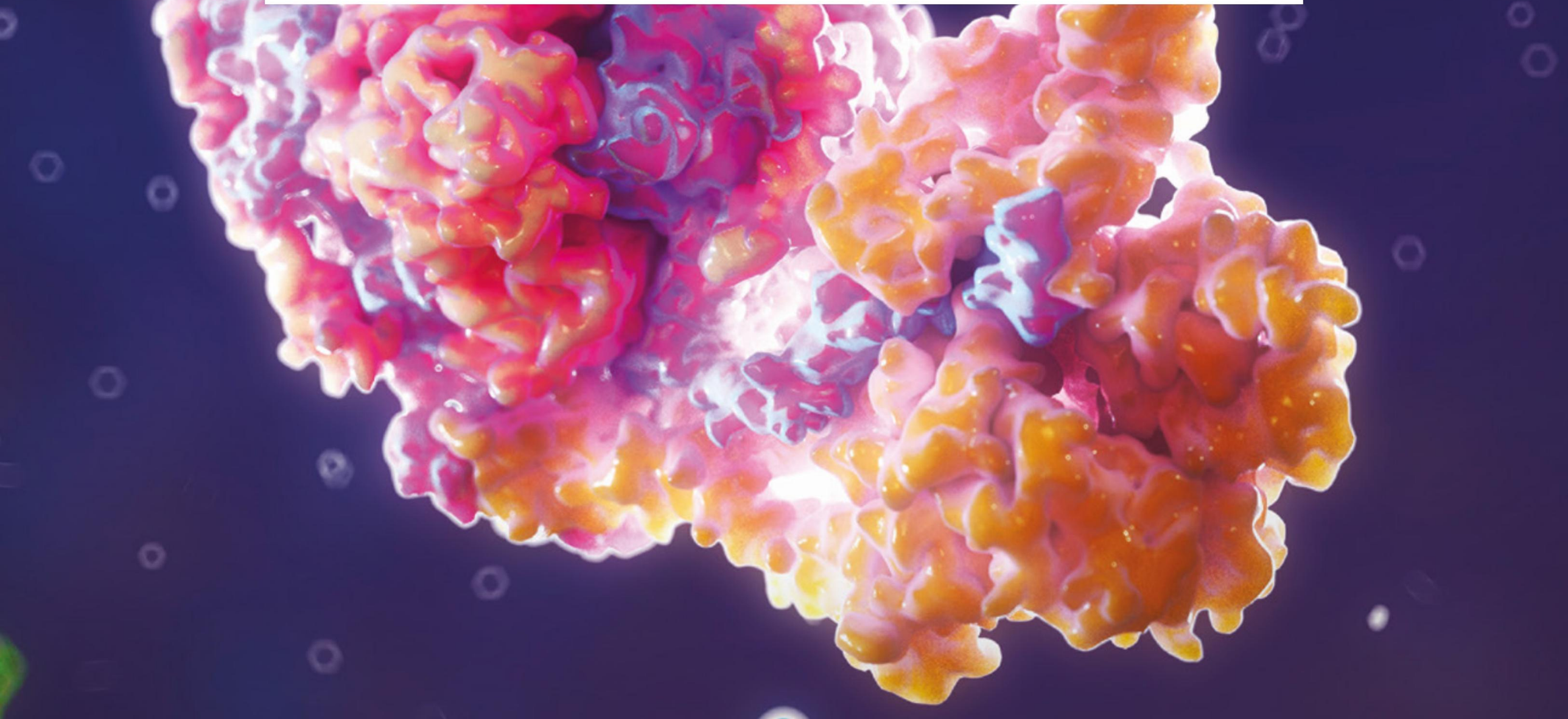

CHAPTER

08 Structure and physical properties of organic compounds

Organic chemistry is the study of carbon-based compounds. With the exception of hydrogen, carbon forms more compounds than all of the other elements put together. In fact, scientists currently know of more than 10 million organic compounds and more are being discovered or synthesised all the time.

Organic compounds exhibit an enormous range of properties, which allows chemists to develop materials for applications as diverse as fuels, fibres, plastics, detergents, dyes, paints, medicines, perfumes and insecticides. Organic compounds also form the basis of all living organisms.

The study of organic chemistry is made easier by grouping organic compounds into classes. In this chapter, you will explore some of the different classes of organic compounds and learn how to identify them. You will examine the different ways in which atoms in organic molecules can be connected using covalent bonds and learn how to represent them using a variety of formulas. You will also learn how to name a range of organic compounds using a set of systematic rules. Finally, you will study the physical properties of various organic compounds and examine how the structures of these compounds determine their properties.

Syllabus subject matter

Topic 1 • Properties and structure of organic materials

STRUCTURE OF ORGANIC COMPOUNDS

- Identify organic molecules including alkanes, alkenes, alkynes, alcohols, aldehydes, ketones, carboxylic acids, haloalkanes, esters, amines and amides. **8.1**
- Discriminate between class and functional groups, e.g. for OH, hydroxyl is the functional group and alcohol is the class. **8.1**
- Describe the features of a homologous series. **8.2**
- Discriminate between saturated and unsaturated organic molecules. **8.1**
- Discriminate between empirical, molecular and structural formulas. **8.1**
- Determine molecular and structural formulas for organic compounds, up to C10, including simple methyl and ethyl branched chains, for
  - alkanes, alkenes and alkynes
  - alcohols (primary, secondary and tertiary)
  - aldehydes and ketones
  - carboxylic acids
  - amines and amides
  - haloalkanes (primary, secondary and tertiary)
  - esters. **8.2, 8.4**

- Apply IUPAC rules in the nomenclature of organic compounds, up to C10, including simple methyl and ethyl branched chains, for
  - alkanes, alkenes and alkynes
  - alcohols (primary, secondary and tertiary)
  - aldehydes and ketones
  - carboxylic acids
  - haloalkanes (primary, secondary and tertiary)
  - esters. **8.2, 8.4**
- Identify structural and stereoisomers, including geometrical (cis and trans) and optical isomers. **8.3**
- Deduce the structural formula of geometrical (cis and trans) isomers (non-cyclic alkenes), optical isomers and isomers of the non-cyclic alkanes up to C6. **8.3**
- Sketch the structural formula and apply IUPAC rules in the nomenclature for isomers of alkanes (non-cyclic) and alkenes (straight chain) up to C6, and for the geometrical (cis and trans) isomers of simple alkenes (non-cyclic). **8.2, 8.3, 8.5**
- Determine the structural formula of optical isomers for simple organic compounds. **8.3**
- Identify chiral carbon atoms. **8.3**

PHYSICAL PROPERTIES AND TRENDS

- Explain the trends (melting point, boiling point, volatility, solubility in water and organic solvents) within and between homologous series (alkanes, alkenes, alcohols and carboxylic acids) in terms of intermolecular and intramolecular bonding, e.g. dispersion forces, dipole–dipole interactions and hydrogen bonds. **8.7, 8.8**
- Analyse data to determine the physical properties of a homologous series, trends in melting point, boiling point, volatility and the solubility of alkanes, alkenes, alcohols and carboxylic acids. **8.7, 8.8**

ORGANIC REACTIONS AND REACTION PATHWAYS

- Determine the primary, secondary and tertiary carbon atoms in haloalkanes and alcohols. **8.4**

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8.1 Diversity of organic compounds

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- define what a functional group is and know that the major classes of organic compounds can be identified by their functional groups
- discriminate between the terms functional group (e.g. hydroxyl) and class (e.g. alcohol)
- discriminate between saturated and unsaturated organic molecules.

Organic chemistry is the study of carbon-based compounds. These compounds make up more than 90% of all chemical compounds and form the basis of all living systems (Figure 8.1.1). Historically, the association with living systems led to the study of carbon compounds being called 'organic chemistry' and the molecules of carbon compounds being referred to as 'organic molecules'. In fact, for a long time, scientists believed that carbon compounds only occurred in living systems, but Friedrich Wöhler disproved this idea in 1828 when he produced urea ($CO(NH_2)_2$) in the laboratory. The definition of organic chemistry now encompasses hydrocarbon-based compounds that originate from living and non-living matter.

In this module, you will be introduced to several different classes of organic compounds. You will also learn how to represent the arrangement of atoms in organic molecules using both structural and condensed formulas.

FIGURE 8.1.1 Different types of organic molecules form the basis of all living systems, including the child, tomatoes, timber and plants in this photograph.

BONDING IN CARBON COMPOUNDS

Why do so many organic compounds exist? To answer this question, we need to understand the bonding properties of carbon.

Carbon atoms contain six electrons—two electrons in the first shell and four in the second. The **electronic configuration** of a carbon atom can be written as 2,4 or $1s^2 2s^2 2p^2$. This means the following:

- Each carbon atom has four **valence electrons**, which gives it a **valence number** of four. The valence number of an element is equal to the number of valence electrons in an atom of that element. All four of carbon's valence electrons are available for bonding with other atoms.
- A carbon atom can form four covalent bonds with up to four other carbon atoms, each of which can also bond with up to four other carbon atoms, thus potentially forming long, branched chains, or even rings.
- Single, double or triple bonds can be formed between two carbon atoms. A molecule that contains only single carbon–carbon bonds is described as a **saturated molecule**. A molecule that contains one or more double or triple carbon-to-carbon bonds is described as an **unsaturated molecule**.
- Single, double or triple bonds can also be formed between carbon atoms and atoms of other elements. For example, carbon can form a single bond with hydrogen, a double bond with oxygen and a triple bond with nitrogen.

REPRESENTING ORGANIC MOLECULES

Before exploring organic molecules further, we will explore the different ways that molecules can be represented in chemical equations and diagrams, such as:

- molecular formulas
- empirical formulas
- extended structural formulas
- condensed structural formulas
- skeletal structures.

Molecular formulas

Molecular formulas, such as C_2H_6O and $C_4H_8O_2$, indicate the number and type of atoms of each element present in a molecule. However, they do not indicate how the atoms are arranged.

Empirical formulas

Empirical formulas are used to show the simplest, whole-number ratio of elements in a compound. You will recall from Unit 1 that empirical formulas are used for ionic compounds, e.g. $MgCl_2$. In organic chemistry, the empirical formula may be different to the molecular formula, e.g. CH_2 is the empirical formula of propene (C_3H_6). The empirical formula is often the first step in determining the molecular formula for an organic compound, as you will discover in Chapter 9.

Extended structural formulas

Extended structural formulas show the location of atoms relative to one another in a molecule, as well as the number and location of covalent bonds.

When four single bonds are formed around a carbon atom, the pairs of electrons in each bond act as a negatively charged cloud. **Valence shell electron pair repulsion (VSEPR)** theory determines that these electron pairs repel each other, so the bonds are as far apart as possible in three dimensions, at an angle to each other of nearly 109.5°. The structure of methane, shown in Figure 8.1.2, is described as a tetrahedral shape because the four single bonds are pointing to the corners of a tetrahedron (shown in red).

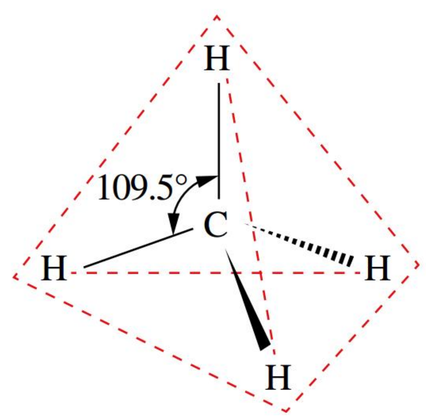


FIGURE 8.1.2 The structure of a molecule of methane (CH_4) showing the tetrahedral geometry. The solid wedge represents a bond coming out of the page, whereas the dashed wedge represents a bond going into the page.

Molecules consisting of long chains of carbon atoms joined by single bonds are often referred to as 'straight-chain' molecules. Because of the tetrahedral distribution of each carbon's bonds, the chain actually has a zigzag shape (Figure 8.1.3a). However, structural formulas showing a tetrahedral arrangement of bonds around carbon atoms can become complicated and difficult to interpret. To make the structure of these molecules clearer, the bonds are often drawn at right angles (Figure 8.1.3b).

Even though there is a tetrahedral arrangement of bonds around each carbon atom, structural formulas are often drawn with the bonds at right angles, for simplicity.

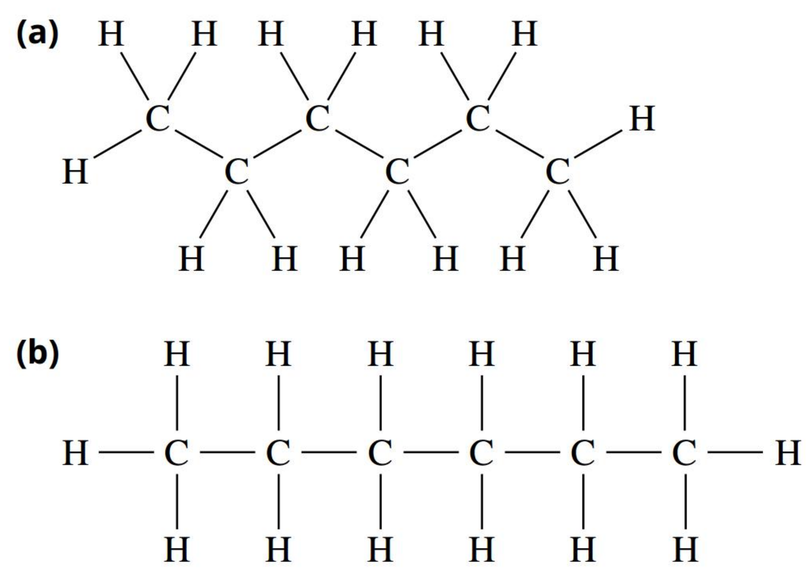


FIGURE 8.1.3 (a) The six-carbon chain of hexane (C_6H_{14}). There is a tetrahedral arrangement of bonds around each carbon atom. (b) The chain can be drawn in a straight line for convenience.

Condensed structural formulas

A **condensed structural formula** is used to indicate the connections in the structure of a compound without showing the three-dimensional arrangement of atoms.

In a condensed structural formula, the carbon chain is represented on one line of text. The carbon atoms in the chain, and all the atoms attached to each of them, are listed in the order that they appear in the structural formula. (Note: the condensed formula can be written from left to right or right to left. So, for example, CH_3NH_2 is the same molecule as NH_2CH_3.) Single bonds are not shown, but double and triple carbon–carbon bonds are often shown. Groups of atoms that form branches in a molecule are written in brackets after the carbon atom to which they are attached.

Chains of $-CH_2$ are often condensed into brackets (as can be seen for butane in Table 8.1.1).

Skeletal structures

A **skeletal structure** is used to represent complex organic molecules. It is a shorthand version of an extended **structural formula**, which shows only the arrangement of carbon–carbon bonds and **functional groups** present in a molecule. A functional group is an atom or group of atoms that largely determines a molecule's properties. In a skeletal structure, the following are left out:

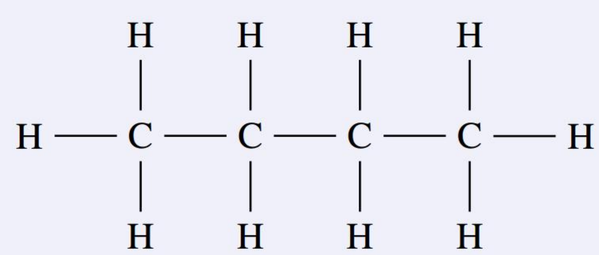
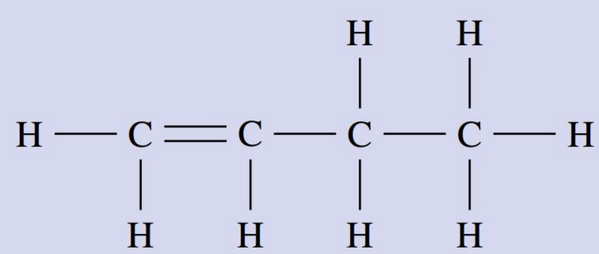
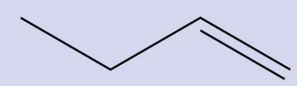
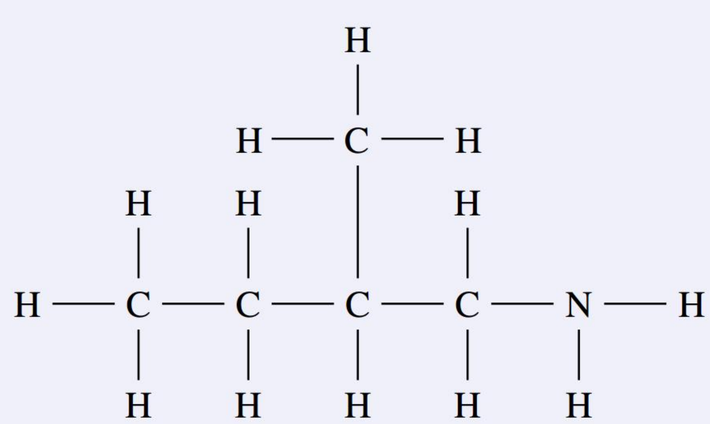
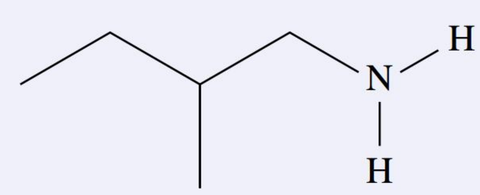
- carbon atoms
- hydrogen atoms attached directly to carbon atoms
- bonds between carbon atoms and hydrogen atoms.

Thus, a skeletal structure includes only the following:

- carbon–carbon single, double and triple bonds
- bonds to functional groups
- bonds within functional groups.

Some examples of molecular, empirical, extended structural and condensed structural formulas, and skeletal structures are shown in Table 8.1.1.

TABLE 8.1.1 Examples of molecular, empirical, extended structural and condensed structural formulas, and skeletal structures

Molecular formula	Empirical formula	Extended structural formula and name	Condensed structural formula	Skeletal structure
C_4H_{10}	C_2H_5	 butane	$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$	
C_4H_8	CH_2	 but-1-ene	$CH_2{=}CHCH_2CH_3$ or $CH_2CHCH_2CH_3$	
$C_5H_{13}N$	$C_5H_{13}N$	 2-methylbutan-1-amine (Note: naming of this class is beyond the scope of this course.)	$CH_3CH_2CH(CH_3)CH_2NH_2$	

A functional group is an atom or group of atoms that largely determines a molecule's properties.

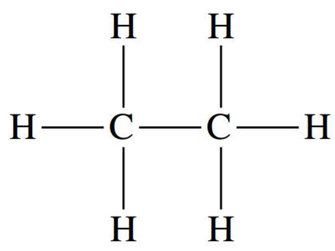


FIGURE 8.1.4 Ethane is a hydrocarbon because it is made up of only carbon and hydrogen.

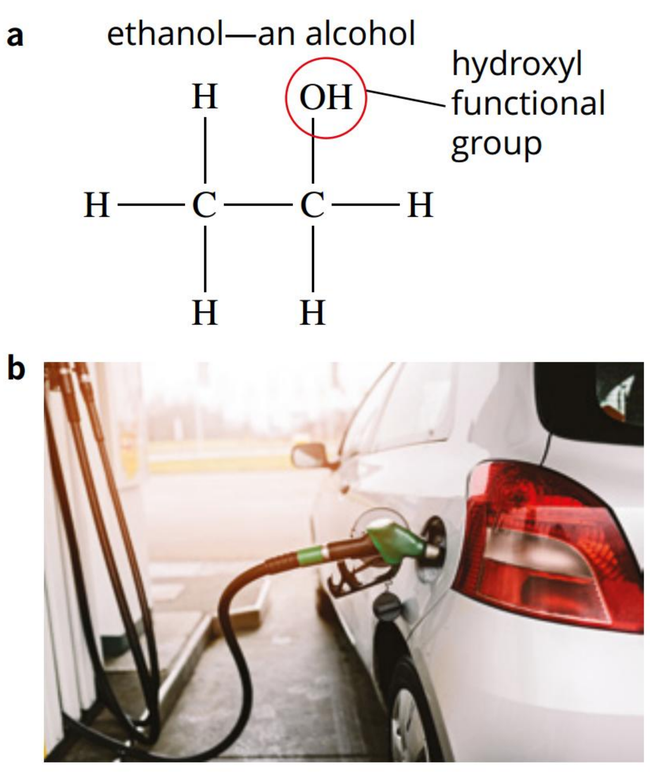


FIGURE 8.1.5 (a) Ethanol belongs to the class of compounds called alcohols. Alcohols contain the hydroxyl (OH) functional group. Note that although this is an extended structural formula, it is common to show features such as functional groups and branches in a condensed form, as shown here. (b) Ethanol is used in alcoholic drinks and as a fuel.

FUNCTIONAL GROUPS

In its many millions of compounds, carbon is almost always associated with hydrogen. Some organic molecules are made up of only carbon and hydrogen, such as ethane, shown in Figure 8.1.4. Molecules made up of only carbon and hydrogen are defined as **hydrocarbons** and you will learn more about them in Module 8.2.

Most organic molecules contain elements in addition to carbon and hydrogen, such as oxygen, nitrogen, sulfur or chlorine. These molecules have a **hydrocarbon skeleton** but one or more of their hydrogen atoms has been replaced with other atoms or groups of atoms called **functional groups**.

A functional group is defined as an atom or a group of atoms that gives a characteristic set of chemical properties to a molecule containing those atoms. The major classes of organic compounds are characterised by their functional groups and several examples are shown in Figures 8.1.5–8.1.7.

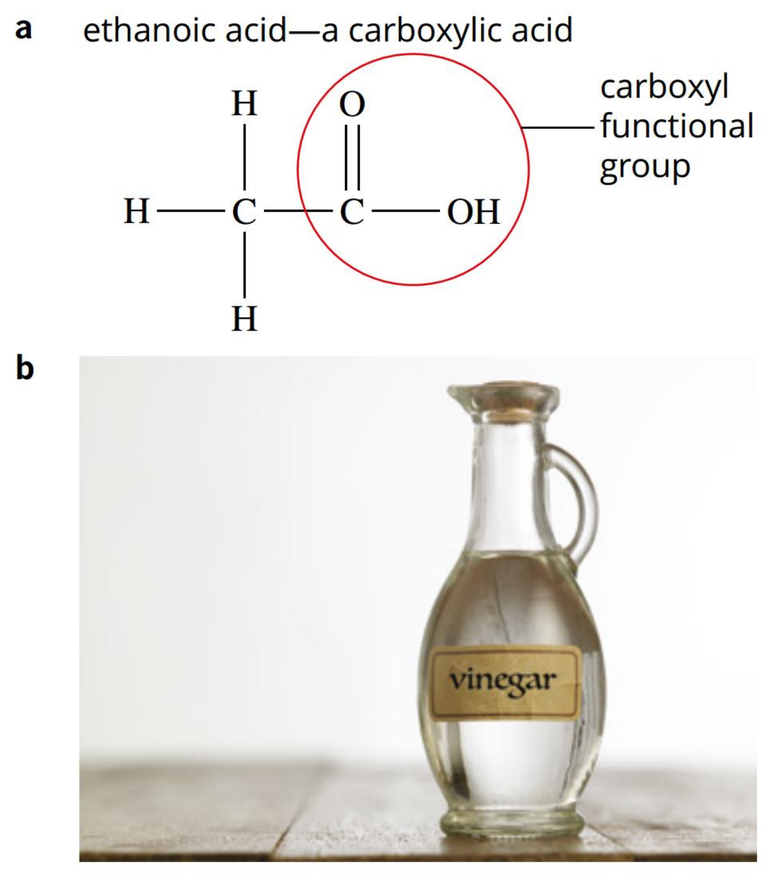


FIGURE 8.1.6 (a) Ethanoic acid belongs to the class of compounds called carboxylic acids. Carboxylic acids contain the carboxyl (COOH) functional group. (b) Ethanoic acid is found in many kinds of foods such as vinegar and tomato sauce. It is also widely used in industry.

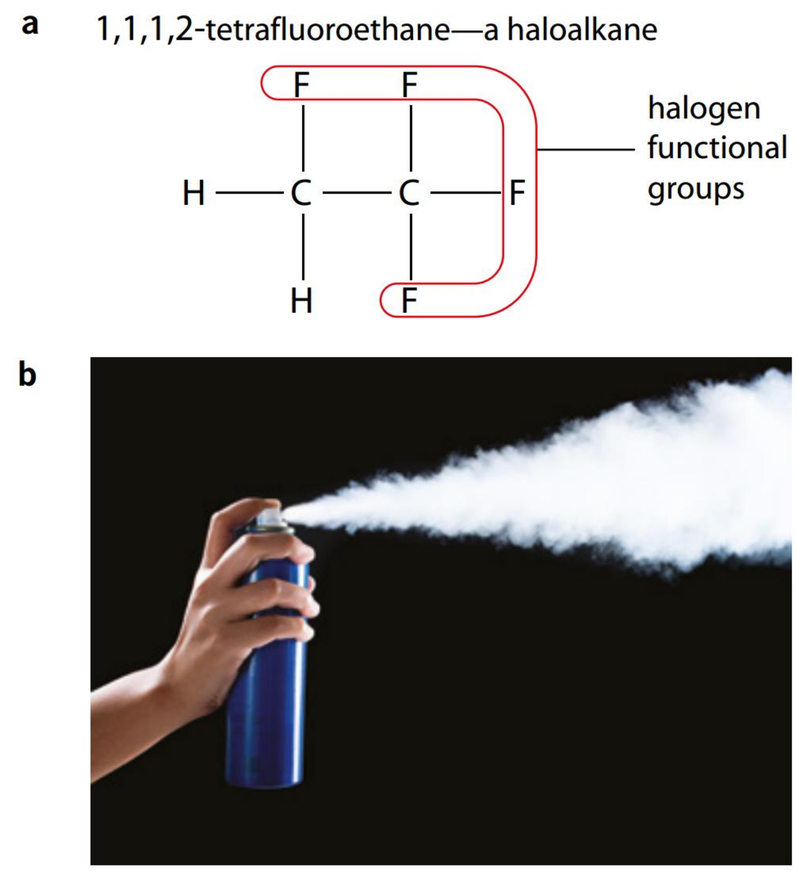
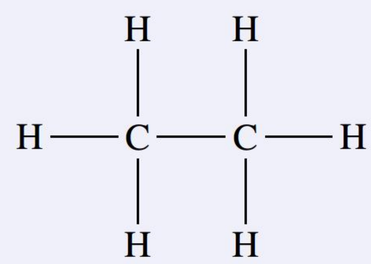
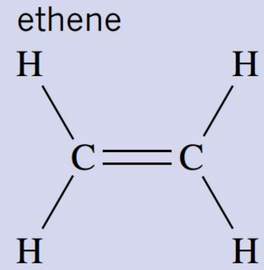
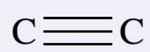
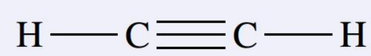
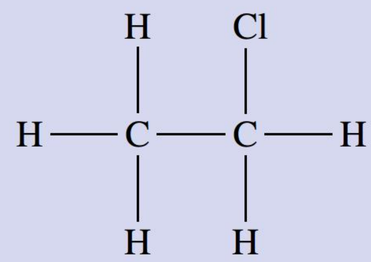
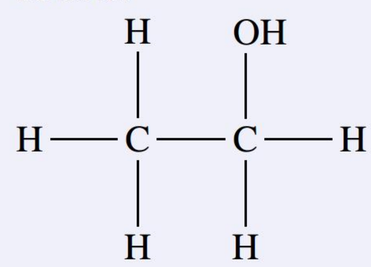
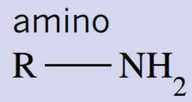
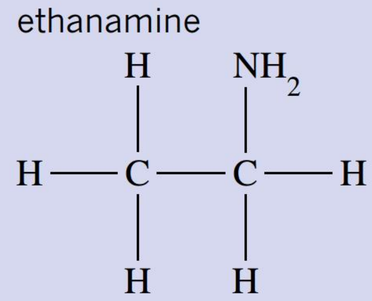
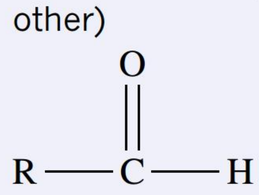
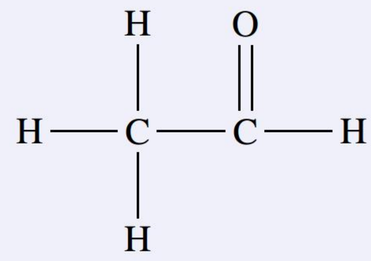
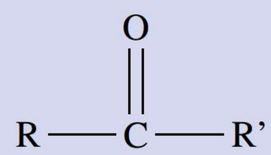
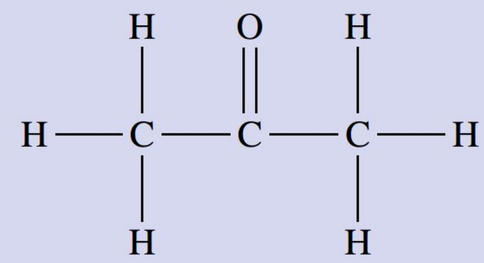
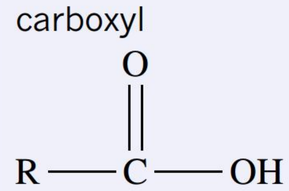
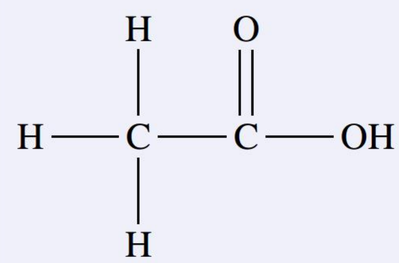
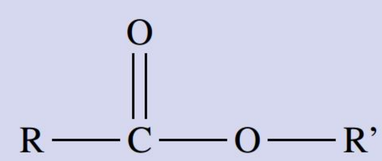
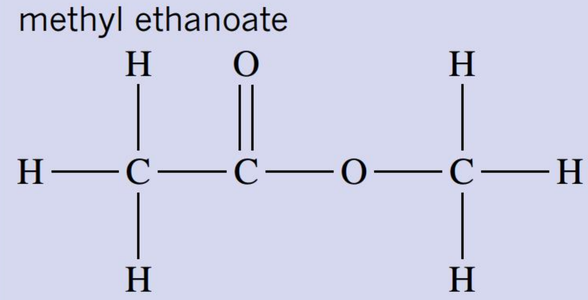
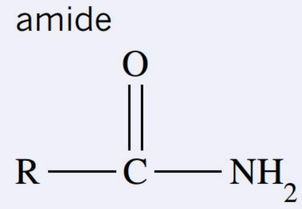
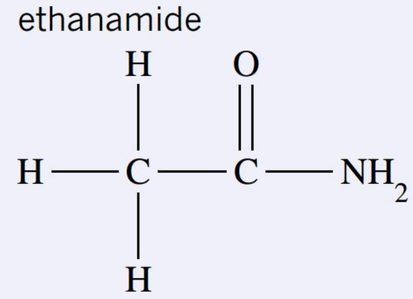


FIGURE 8.1.7 (a) 1,1,1,2-tetrafluoroethane belongs to the class of compounds called haloalkanes. Haloalkanes contain a halogen atom as their functional group. (b) 1,1,1,2-tetrafluoroethane is widely used as a refrigerant and in aerosols.

Table 8.1.2 gives a summary of the major classes of organic compounds and shows the functional groups that characterise each class. Note that the symbols R and R' usually represent the hydrocarbon chain that makes up the rest of the organic molecule, but they can also be used to represent any group of atoms. It is important to realise that even though **alkenes** and **alkynes** are hydrocarbons, their double and triple bonds are still considered to be functional groups because the multiple bonds are responsible for each class's chemistry. You will learn more about different classes of organic compounds in Modules 8.2 and 8.4.

TABLE 8.1.2 Summary of the major classes of organic compounds

Class of organic compound	Functional group present	Example
alkane	none	ethane 
alkene	carbon-to-carbon double bond	ethene 
alkyne	carbon-to-carbon triple bond 	ethyne 
haloalkane	halogen (where X = F, Cl, Br, I)	chloroethane 
alcohol	hydroxyl	ethanol 
amine	amino 	ethanamine 
aldehyde	carbonyl (C=O) (attached to a hydrogen atom on one side and the carbon of an R group on the other) 	ethanal 

Class of organic compound	Functional group present	Example
ketone	carbonyl (C=O) (attached to carbon atoms of the R groups on either side) 	propanone 
carboxylic acid	carboxyl 	ethanoic acid 
ester	ester 	methyl ethanoate 
amide	amide 	ethanamide 

8.1 Review

SUMMARY

- Organic compounds can be represented as a molecular formula, empirical formula, extended structural formula, condensed structural formula or as a skeletal structure.
- Organic chemistry is the study of carbon-based compounds.
- Carbon atoms can form covalent bonds with each other to create long chains or rings.
- Carbon atoms can form single, double or triple bonds with other carbon atoms as well as other non-metallic atoms such as hydrogen, oxygen or nitrogen.
- In its many millions of compounds, carbon is almost always associated with hydrogen, giving organic molecules a hydrocarbon skeleton.
- A saturated molecule is one that contains only single carbon–carbon bonds.
- An unsaturated molecule contains one or more double or triple carbon-to-carbon bonds.
- A functional group is an atom or a group of atoms that gives a characteristic set of chemical properties to a molecule containing those atoms.
- Organic compounds can be grouped into classes.
- The many classes of organic compounds are characterised by their functional groups.

KEY QUESTIONS

Describe

1 Define the following terms.

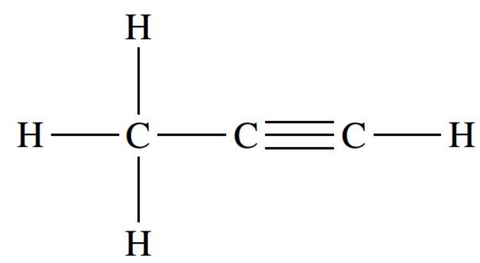
a saturated molecule

b functional group

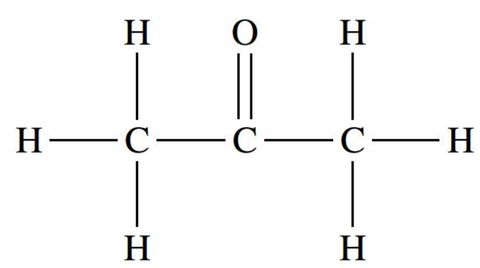
c alcohol

2 Identify the functional groups in each of the following compounds.

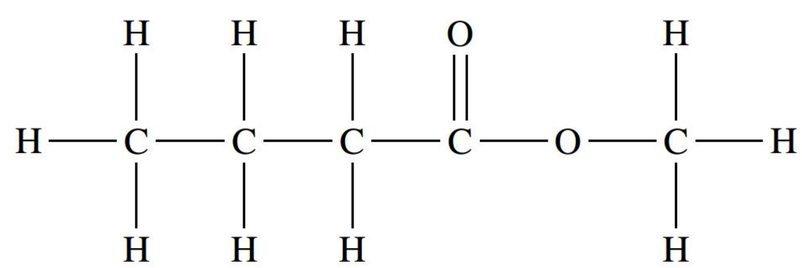
a



b



c



Apply

3 **a** Explain the difference between the organic classes of amines and amides.

b Draw an amine with three carbon atoms.

c Draw an amide with two carbon atoms.

4 Methane is the smallest hydrocarbon molecule.

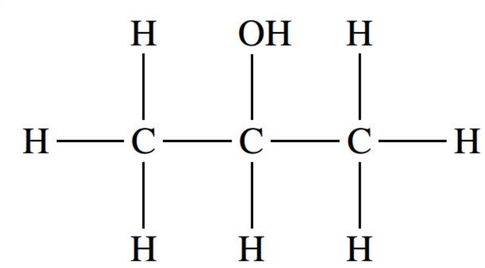
a Describe why methane is termed a hydrocarbon.

b Explain why the carbon atom in a methane molecule bonds to four hydrogen atoms, rather than two, three, five or any other number of hydrogen atoms.

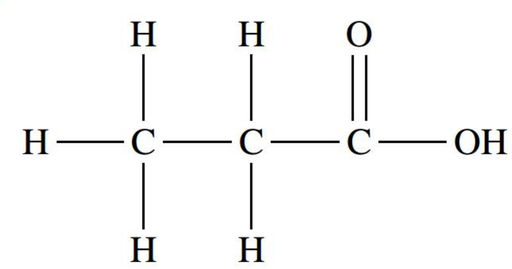
Analyse

5 Analyse the following molecules. Identify the functional group in each and categorise each molecule into a class based on its functional group.

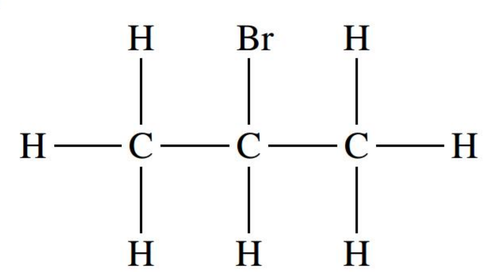
a



b



c



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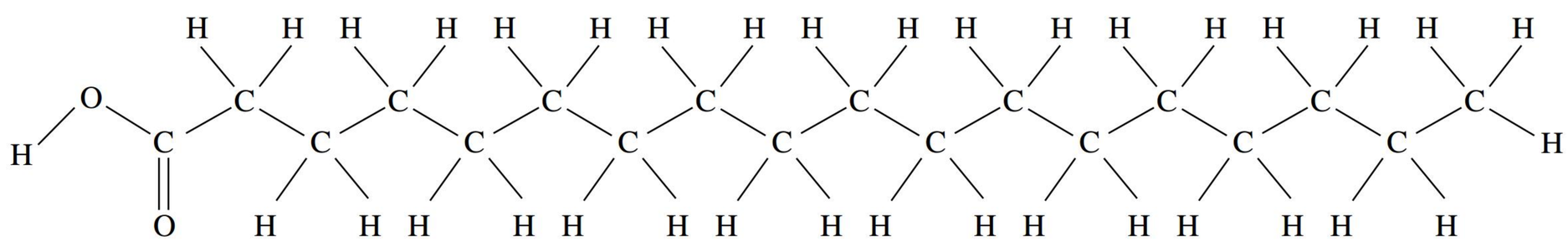
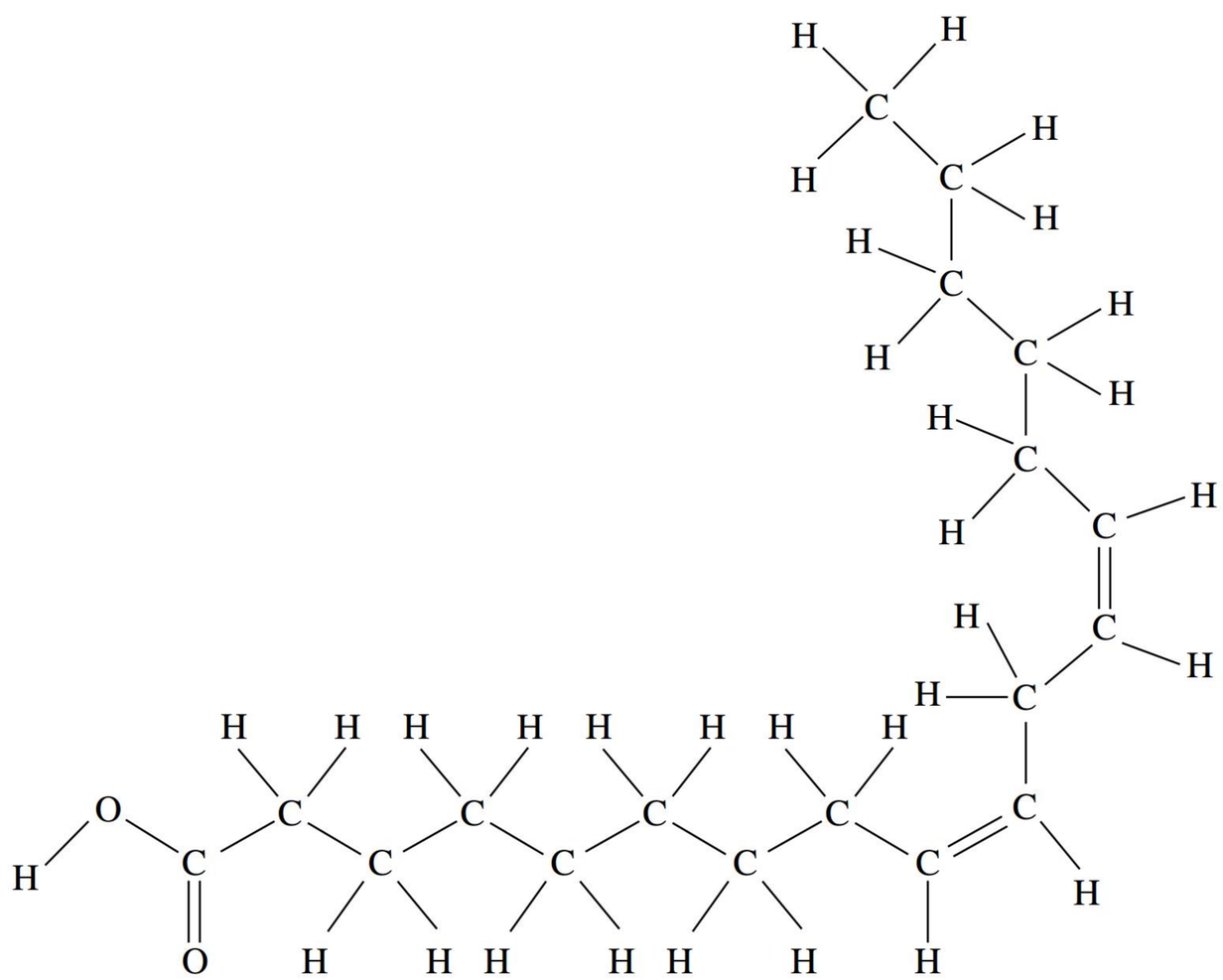
8.1 Review *continued*

6 Categorise the following molecules as saturated or unsaturated.

a

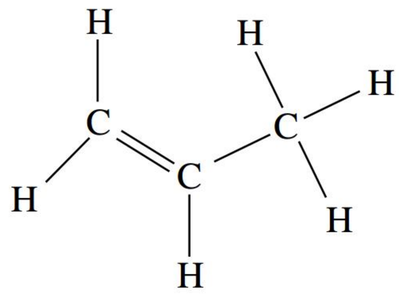
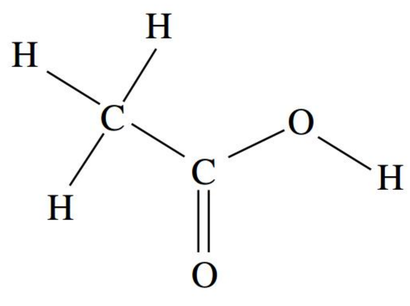


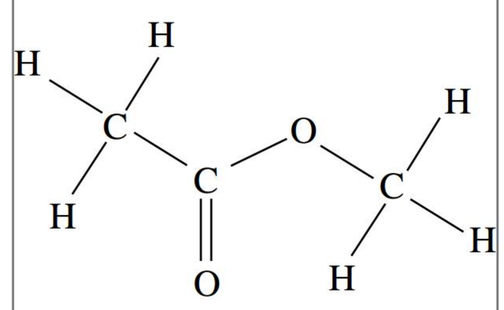
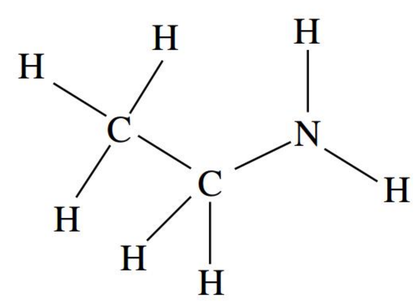
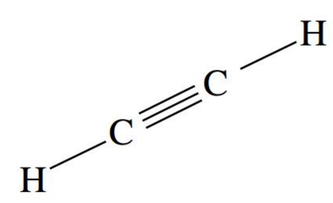
b



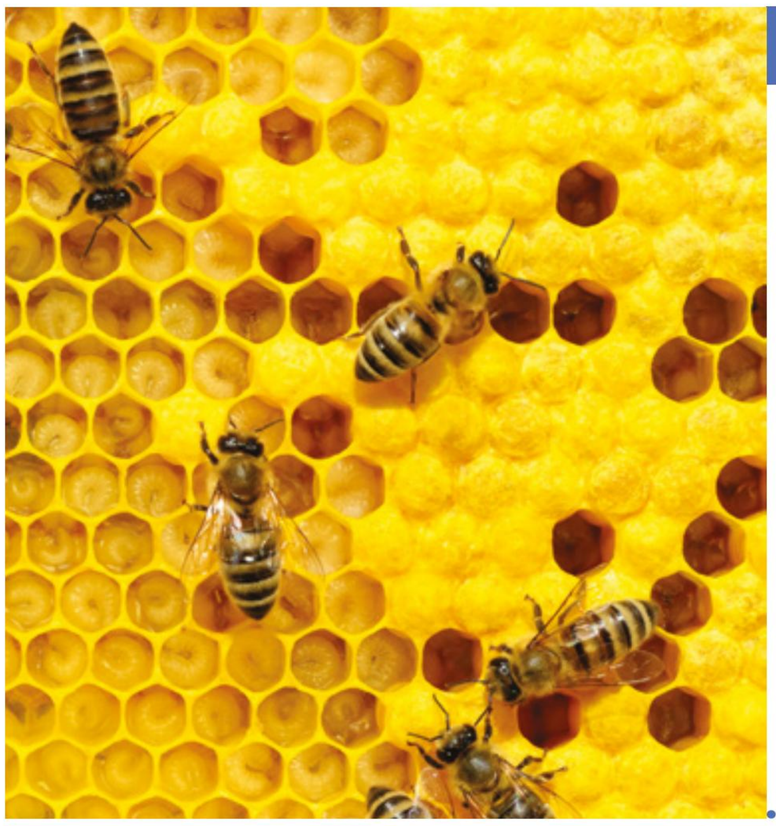
c CH_2CH_2

7 Complete the table below.

	Molecular formula	Structural formula	Condensed structural formula	Class of compound	Name of functional group present
a	C_3H_6		CH_2CHCH_3 or $CH_2{=}CHCH_3$		
b				carboxylic acid	

	Molecular formula	Structural formula	Condensed structural formula	Class of compound	Name of functional group present
c					ester
d				amine	
e	C_3H_7NO		$CH_3CH_2CONH_2$		amide
f				alkyne	

8.2 Hydrocarbons



BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- define hydrocarbons and know the main classes are alkanes, alkenes and alkynes
- define homologous series and understand that members of the same homologous series have a similar structure, the same pattern to their physical properties, the same chemical properties and the same general formula
- describe alkanes, alkenes and alkynes in terms of their structure and general formulas
- use systematic naming rules to name alkanes, alkenes and alkynes
- represent alkanes, alkenes and alkynes using empirical, molecular, condensed structural and extended structural formulas when given their systematic names.

Hydrocarbons are organic compounds that are composed only of carbon and hydrogen.

The simplest organic molecules are the hydrocarbons. Hydrocarbons are organic compounds that are composed only of carbon and hydrogen. Although hydrocarbons contain just these two elements, the different ways their atoms can be arranged to form molecules results in an enormous diversity of compounds.

Most hydrocarbons are produced from **crude oil**, which is also called **petroleum**. Crude oil is a liquid found in Earth's crust that has been formed over millions of years by the effects of heat and pressure on dead animals, plants and microorganisms trapped beneath sediment. Crude oil, shown in Figure 8.2.1, contains a complex mixture of hydrocarbons and is the source of many hydrocarbons used in industry.

FIGURE 8.2.1 Crude oil burning in a Petri dish

Organic compounds can be grouped into several classes called **homologous series**. A homologous series is a class of molecules in which each member differs by $-CH_2-$ from the previous member. Homologous series contain members that have increasingly longer chains. Compounds that are members of the same homologous series have:

- a similar structure
- a pattern to their physical properties
- similar chemical properties
- the same general formula.

In this module, you will study three homologous series that are all hydrocarbons, the **alkanes**, alkenes and alkynes. You will examine the structure of the molecules in each series and look at the ways in which the molecules can be represented using molecular, extended structural and condensed structural formulas. You will also learn how to name the molecules in each series using a set of systematic rules.

SATURATED HYDROCARBONS

Alkanes

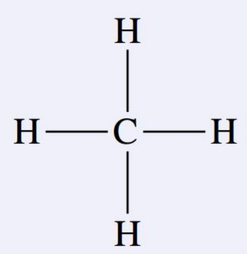
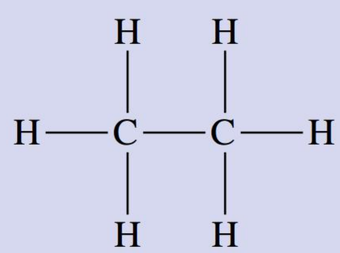
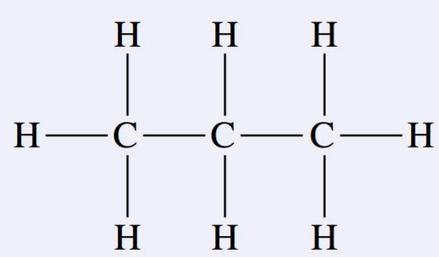
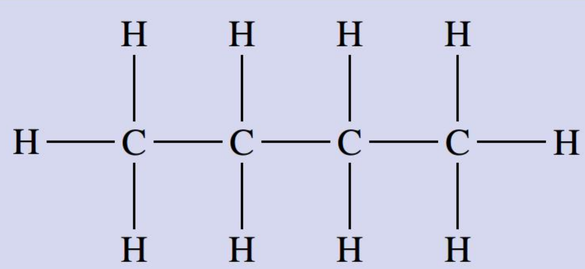
Alkanes are saturated hydrocarbons; they contain only single carbon–carbon bonds.

Methane is the simplest hydrocarbon; you were introduced to methane in Module 8.1. As shown in Table 8.2.1, methane contains one carbon atom covalently bonded with four hydrogen atoms to form a molecule with the formula CH_4. Methane is the first of the homologous series of compounds known as the alkanes. Alkanes are hydrocarbons that contain only single covalent bonds and are therefore described as being saturated. Alkanes have the general formula C_nH_{2n+2}.

The formulas and uses of the first four members of the alkanes are shown in Table 8.2.1. You can see that successive members differ by a $-CH_2-$ unit and that

each alkane follows the general formula C_nH_{2n+2}, where n represents the number of carbon atoms. Because the carbon atoms in alkanes are surrounded by four single bonds, the shape around each carbon atom is **tetrahedral**. However, to make the structures easier to interpret, the structural formulas are drawn so that the bonds are shown at right angles.

TABLE 8.2.1 Formulas and uses of the first four members of the alkanes

Name	Structural formula	Condensed structural formula	Molecular formula	Empirical formula	Uses
methane		CH_4	CH_4	CH_4	cooking, Bunsen burners, gas heating
ethane		CH_3CH_3	C_2H_6	CH_3	conversion to ethene for the production of plastics
propane		$CH_3CH_2CH_3$	C_3H_8	C_3H_8	liquid petroleum gas (LPG)
butane		$CH_3CH_2CH_2CH_3$	C_4H_{10}	C_2H_5	fuel for cigarette lighters, aerosol propellant

Naming alkanes

The systematic naming of organic compounds is controlled by the **International Union of Pure and Applied Chemistry (IUPAC)**. Under the IUPAC system, the name of the compound provides details of its structure. Learning to name the alkanes is important because the rules for naming all other organic compounds are based on the alkane names.

Naming simple alkanes

In the systematic name of simple 'straight-chain' alkanes, the **stem name** refers to the number of carbon atoms in the alkane molecule. Consider propane, which is the alkane in Table 8.2.1 with three carbon atoms. The stem name in propane (prop-) indicates there are three carbon atoms in the molecule. This same stem name is used in other series for the compound that contains three carbon atoms in the main chain. The stem names used for molecules with between one and ten carbon atoms are listed in Table 8.2.2.

The names of all alkanes have the suffix (ending) '-ane' to indicate that the carbon–carbon bonds are all single bonds. Consider again the alkanes listed in Table 8.2.1. Combining the stem name and suffix, you can see that methane is an alkane that contains one carbon atom, ethane is an alkane that contains two carbon atoms, propane is an alkane that contains three carbon atoms and butane is an alkane that contains four carbon atoms.

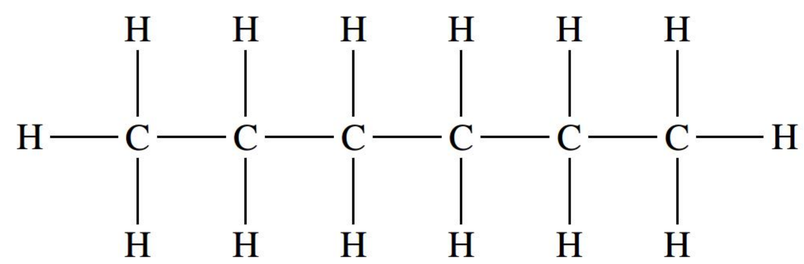
TABLE 8.2.2 Stem names used for molecules with between one and ten carbon atoms

Stem name	Number of carbon atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Worked example 8.2.1

NAMING ALKANES

Represent the following alkane by its systematic name and molecular formula.

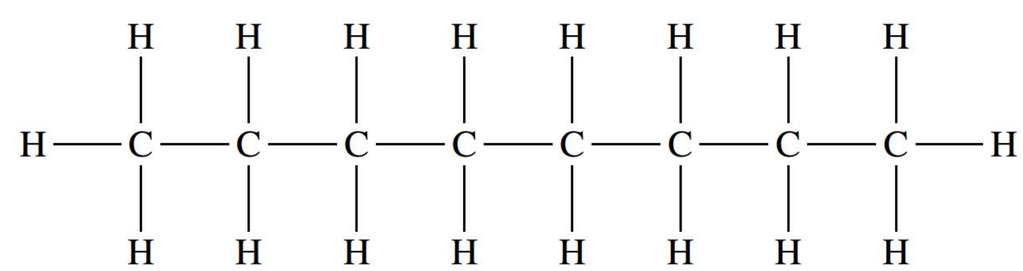


Thinking	Working
Count the number of carbon atoms in the chain to identify the stem name.	There are six carbon atoms, so the stem name will be 'hex'.
Identify the suffix name.	As the compound is an alkane, the suffix will be '-ane'.
Combine the stem name and suffix (the stem comes first).	The systematic name of the alkane is hexane.
The general formula of an alkane is C_nH_{2n+2}, where n = number of carbon atoms. As this alkane has six carbon atoms, substitute 6 for n in the general formula.	As the alkane molecule has six carbon atoms, the number of hydrogens will be: $2n + 2 = (2 \times 6) + 2 = 14$ The molecular formula is C_6H_{14}.

➤ Try yourself 8.2.1

NAMING ALKANES

Represent the following alkane by its systematic name and molecular formula.



Naming branched alkanes

With the first three alkanes—methane, ethane and propane—there is only one way in which the carbon atoms can be arranged and that is in a straight-chain arrangement. This is shown in Figure 8.2.2.

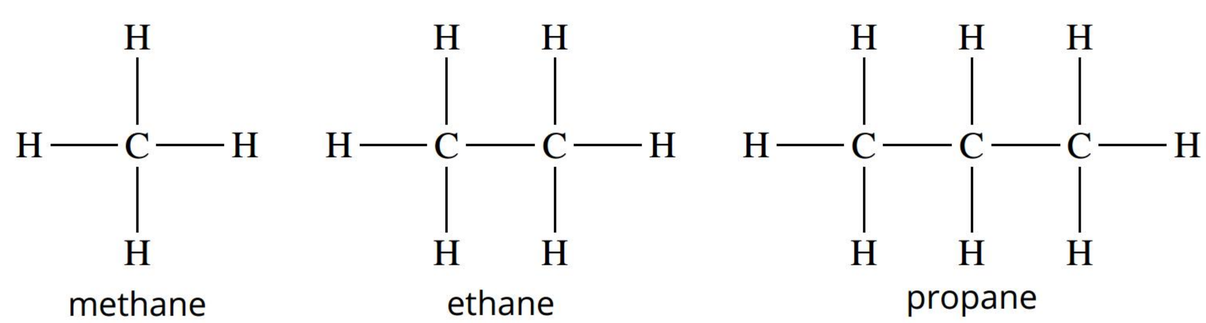


FIGURE 8.2.2 The carbon atoms in methane, ethane and propane can only be arranged in one way—a straight-chain arrangement.

However, when the number of carbon atoms in the alkane reaches four or above, then the carbon atoms can be arranged differently. Figure 8.2.3 shows two different molecules that have the molecular formula C_4H_{10}. Molecules that have the same molecular formula but different structures are known as **structural isomers**. You will learn more about structural isomers in Module 8.3.

Alkanes with four or more carbon atoms can have different arrangements. Figure 8.2.3a shows the straight-chain alkane butane, so named because the four

carbon atoms are bonded in a continuous chain. Figure 8.2.3b is a branched alkane with a $-CH_3$ group attached. A $-CH_3$ group is called a methyl group, as its structure is similar to that of methane with one less hydrogen. The alkane shown in Figure 8.2.3b is named 2-methylpropane, as it can be regarded as a propane molecule with a methyl group attached to the second carbon atom in the propane chain. Note that single carbon–carbon bonds are all the same length, but sometimes longer carbon–carbon bonds are drawn for convenience, such as in the structure of 2-methylpropane shown here.

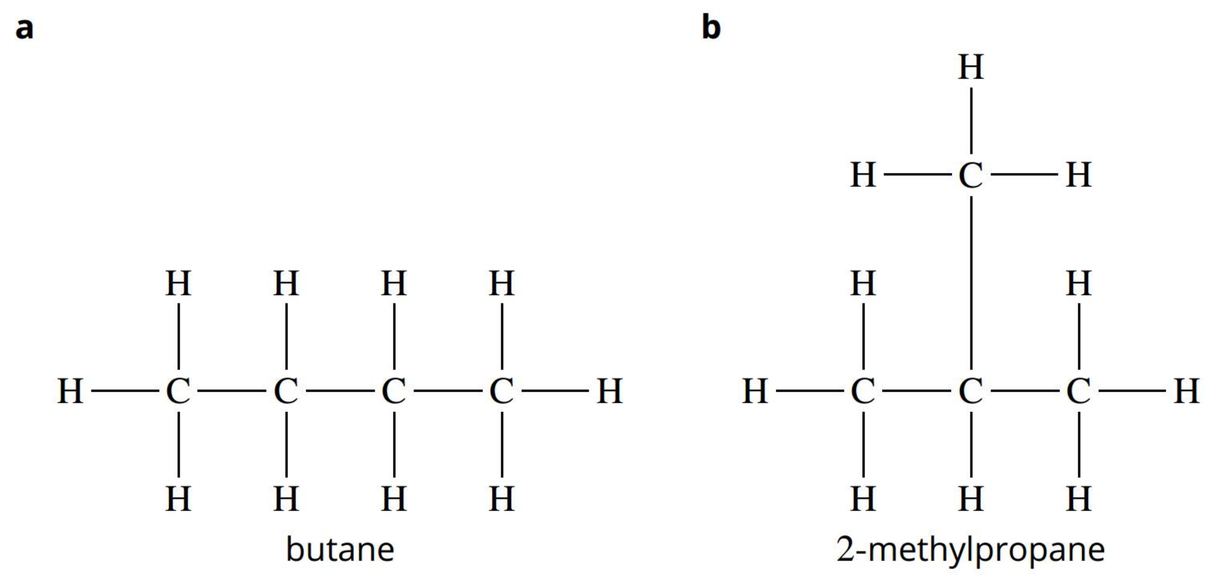


FIGURE 8.2.3 (a) Straight-chain alkane butane; (b) a branched alkane with a $-CH_3$ group attached

A methyl group is an example of an **alkyl side chain.** Alkyl side chains have one less hydrogen atom than the corresponding alkane of the same name. To name an alkyl side chain, take the name of the alkane from which the side chain is derived, drop the suffix '-ane' and add '-yl'. The names of the alkyl side chains with one or two carbon atoms are listed in Table 8.2.3.

TABLE 8.2.3 Names of alkyl side chains

Alkyl side chain	Corresponding alkane	Name of alkyl side chain
$-CH_3$	methane	methyl
$-CH_2CH_3$	ethane	ethyl

Rules for naming alkanes

It would be useful to have a short set of rules to assist us when naming any of the alkanes, no matter whether you are dealing with straight-chain or branched alkanes. Fortunately, all but the most complicated alkanes can be named using the following steps.

1. Identify the longest continuous carbon chain. This is the **parent alkane**. Carefully check which is the longest chain because sometimes it is not drawn in a straight line.
2. Number the carbon atoms in the chain from the end nearest the first branch point (so that the first alkyl side chain will have the smallest number).
3. Name the alkyl side chains after the alkane from which they are derived.
4. Place the number and position of each of the alkyl side chains before the parent alkane's name.
5. If two identical side chains are present, use 'di-' as a prefix; for three, use 'tri-'. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas.
6. If there are alkyl side chains of different lengths on the molecule, list them in alphabetical order at the start of the name. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas.
7. Write the name as a single word with hyphens to separate numbers from letters and commas to separate numbers.

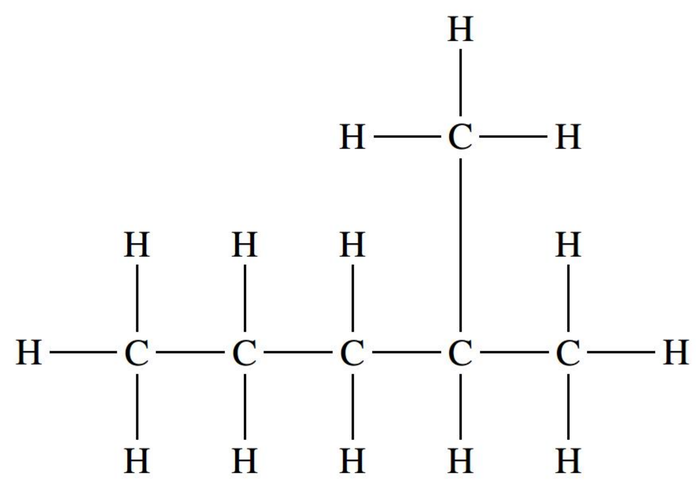
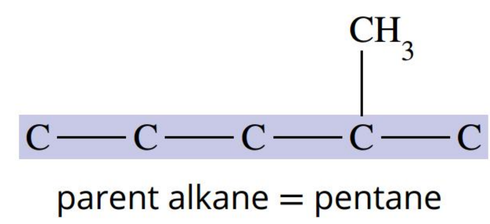


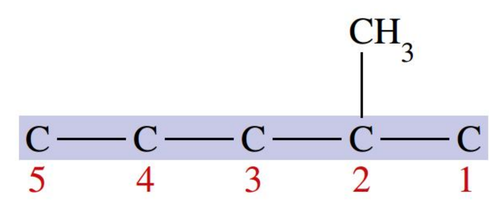
FIGURE 8.2.4 The IUPAC system will be used to name this branched alkane.

The following steps show the process of naming the branched alkane shown in Figure 8.2.4.

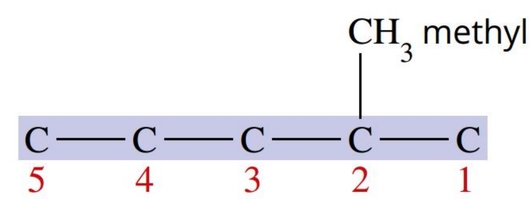
1. Identify the longest continuous carbon chain. This is the parent alkane.



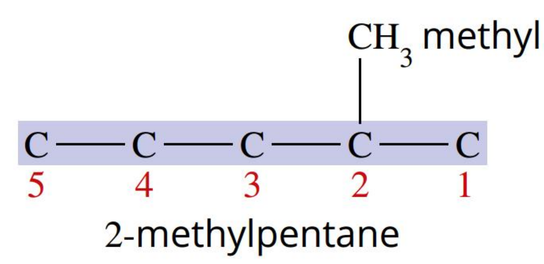
2. Number the carbon atoms from the end of the chain nearest the first branch point.



3. Name the alkyl side chains after the alkane from which they are derived.



4. Place the number and position of each of the alkyl side chains before the parent alkane's name.



Rules 5 and 6 are not required for this example.

5. Write the name as a single word with hyphens to separate numbers from letters and commas to separate numbers. The name of the compound is 2-methylpentane.

Figure 8.2.5 shows further examples of the application of these rules. There are a few important points to note about these examples.

1. Figures 8.2.5a and b show identical molecules even though their structures may appear different at first glance. This is because the longest chain in Figure 8.2.5b has not been drawn in a straight chain as it has in Figure 8.2.5a.
2. In Figure 8.2.5c, note the use of the prefix 'di-' to indicate the presence of two methyl side chains and the numbering to indicate the position of each of these side chains along the longest continuous carbon chain (the 2,2- indicates that both side chains come off the second carbon atom).
3. In Figure 8.2.5d, there are two different alkyl side chains, the methyl side chain on carbon number 2 and the ethyl side chain on carbon number 3. When two or more different side chains are present, they should be listed in alphabetical order in the name of the compound.

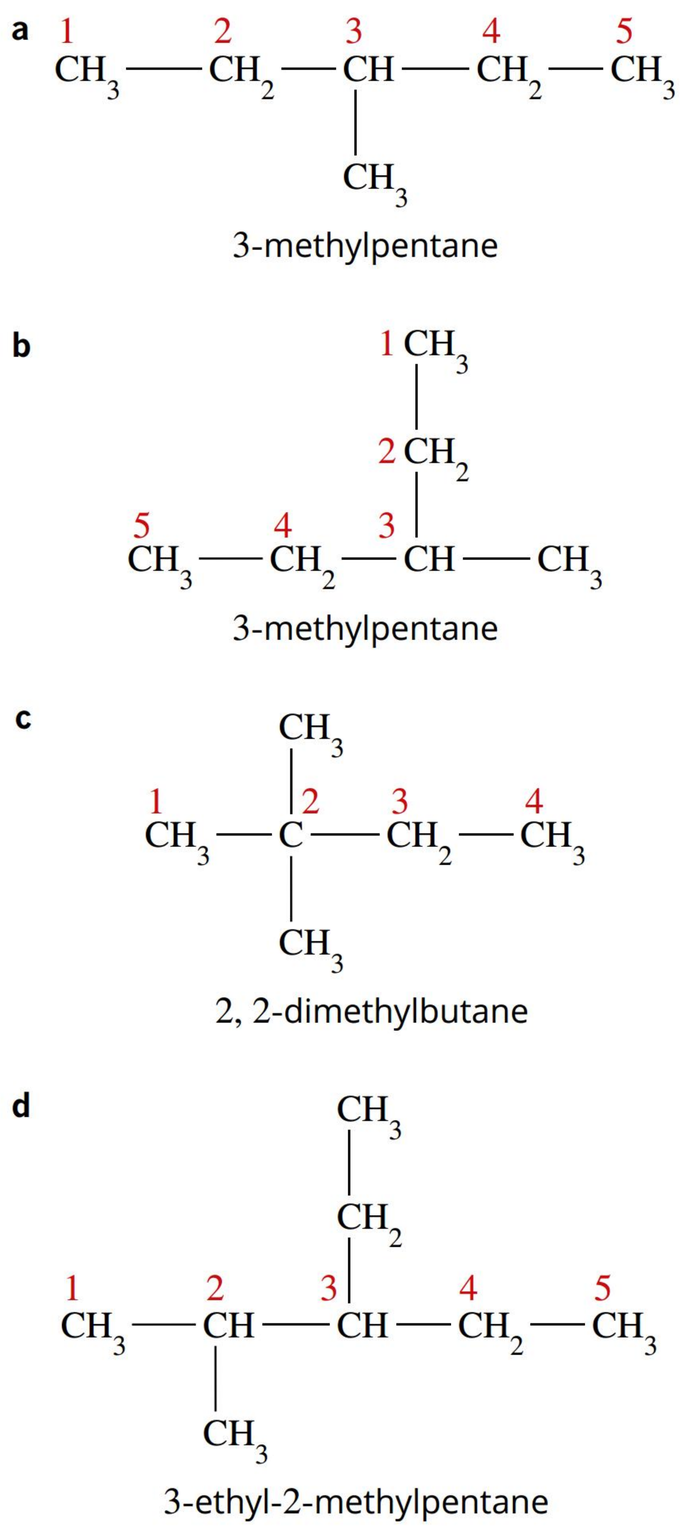
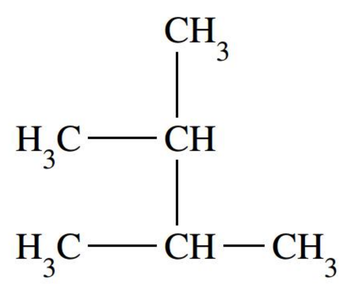


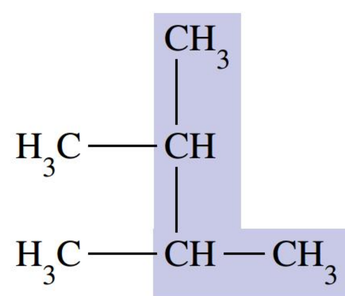
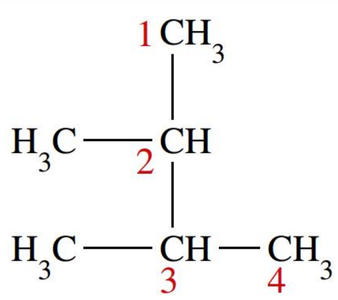
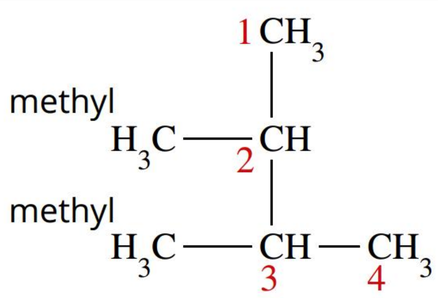
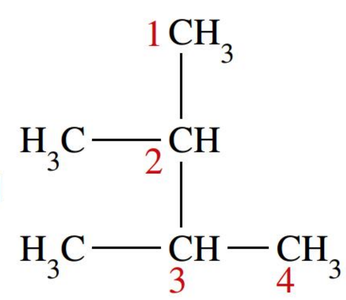
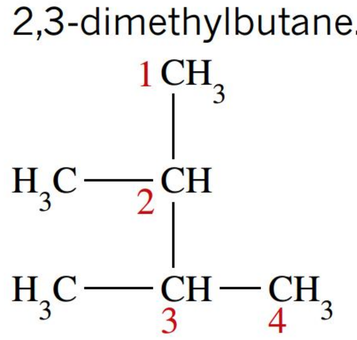
FIGURE 8.2.5 IUPAC systematic names for four alkanes. Note that there are no spaces in the names of these compounds.

Worked example 8.2.2

NAMING BRANCHED ALKANES

Analyse the following alkane and determine its systematic name.

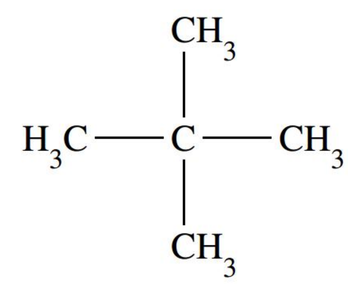


Thinking	Working
Identify the longest continuous carbon chain; this is the parent alkane. In this case, the longest continuous carbon chain is not the chain that is drawn in a straight line.	 4 carbons = butane parent alkane = butane
Number the carbon atoms from the end of the chain nearest the first branch point. Note that in this case, it does not matter which end we start from; the two alkyl side chains appear on carbon numbers 2 and 3, respectively.	
Name the alkyl side chains after the alkane from which they are derived.	 methyl methyl
Place the number and position of each of the alkyl side chains before the parent alkane's name. In this case, because two identical side chains are present, use 'di-' as a prefix.	 2,3-dimethyl
Represent the name as a single word with hyphens to separate numbers from letters and commas to separate numbers.	The name of the compound is 2,3-dimethylbutane. 

➤ Try yourself 8.2.2

NAMING BRANCHED ALKANES

Analyse the following alkane and determine its systematic name.



UNSATURATED HYDROCARBONS

Carbon forms many compounds with hydrogen in which there are double or even triple bonds between the carbon atoms. These compounds are called unsaturated hydrocarbons. A double bond is formed when two pairs of electrons are shared and a triple bond is formed when three pairs of electrons are shared. Some of the most useful carbon compounds are unsaturated. This module focuses on the structures and naming of hydrocarbon compounds with carbon–carbon double bonds and triple bonds.

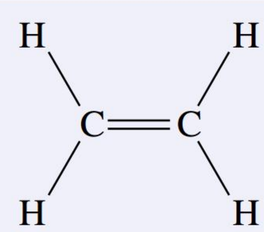
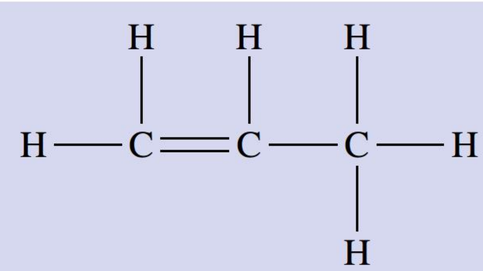
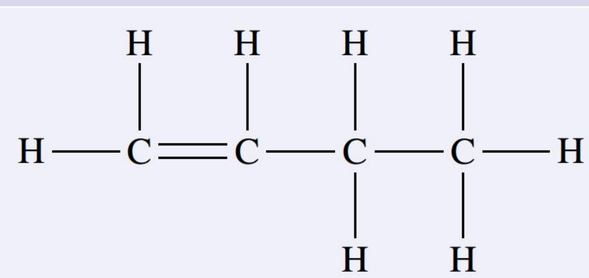
Alkenes

Alkenes are unsaturated hydrocarbons that contain one carbon–carbon double bond.

Alkenes are a homologous series of hydrocarbons with one carbon–carbon double bond. The carbon–carbon double bond is a functional group that gives alkenes their chemical properties and makes them much more reactive than alkanes. Alkenes with one carbon–carbon double bond have the general formula C_nH_{2n}.

The formulas and uses of the first three members of the homologous series of alkenes are shown in Table 8.2.4. You can see that successive members differ by a $-CH_2-$ unit and that each alkene follows the general formula C_nH_{2n}, where n represents the number of carbon atoms. The shape around each carbon atom in the double bond is trigonal planar; however, to make the structures easier to interpret, the structural formulas are often drawn so that the bonds are shown at right angles.

TABLE 8.2.4 Formulas of the first three members of the alkene homologous series

Name	Molecular formula	Extended structural formula	Condensed structural formula	Uses
ethene	C_2H_4		$CH_2{=}CH_2$	in the manufacture of a wide range of chemicals
propene	C_3H_6		$CH_2{=}CHCH_3$	in the manufacture of propene oxide and polymers
but-1-ene	C_4H_8		$CH_2{=}CHCH_2CH_3$	in the manufacture of butanol and polymers

Naming alkenes

The rules for naming alkenes follow the same general rules used for naming alkanes. However, there are a few differences, which are outlined below.

- Use '-ene' as the suffix for the parent name.
- Number the carbon atoms from the end of the chain closest to the double bond.
- Specify the position of the double bond by the number of the lowest-numbered carbon atom in the double bond.
- Insert the number into the name immediately before '-ene'.

The following steps show the process of naming the alkene in Figure 8.2.6.

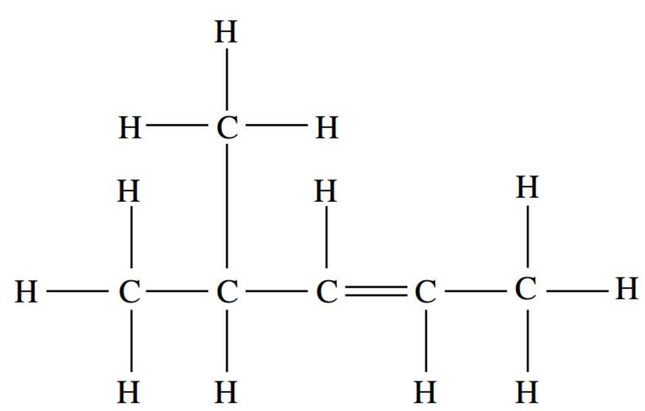
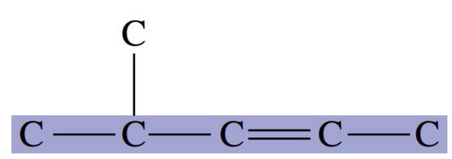


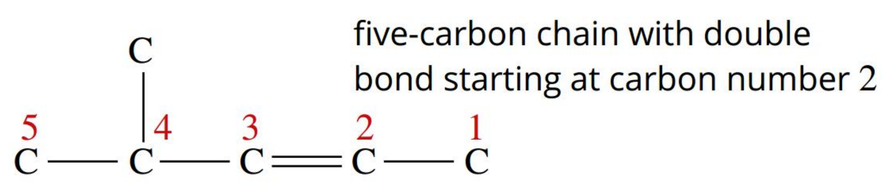
FIGURE 8.2.6 The IUPAC system will be used to name this alkene.

1. Identify the longest continuous carbon chain that contains the double bond. The name of the molecule is based on this chain.



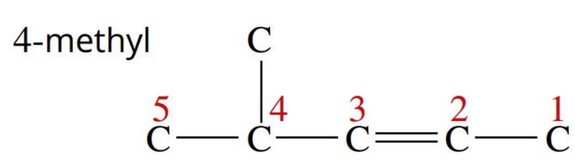
   - It is a five-carbon chain, so the name of the molecule is based on pentene.

2. Number the carbons, starting from the end closest to the double bond. Note the position of the double bond.



   - It is a five-carbon chain with the double bond starting at carbon number 2. The parent name is therefore pent-2-ene.

3. Name each alkyl side chain and identify the number of the carbon atom in the main chain that each is attached to.



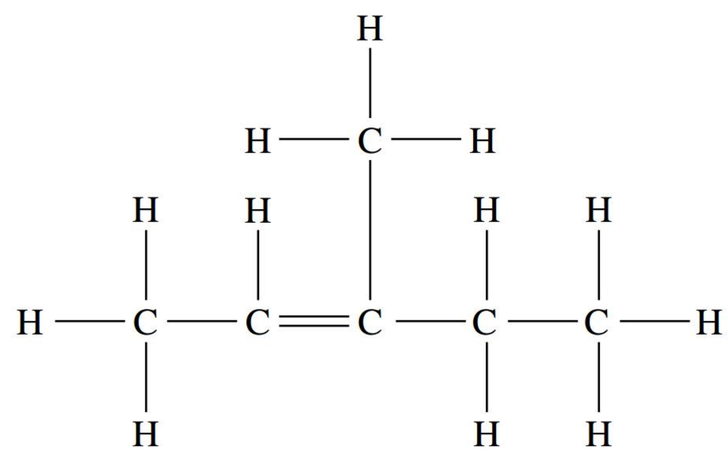
   - There is a methyl group on carbon number 4. It will be named as 4-methyl.

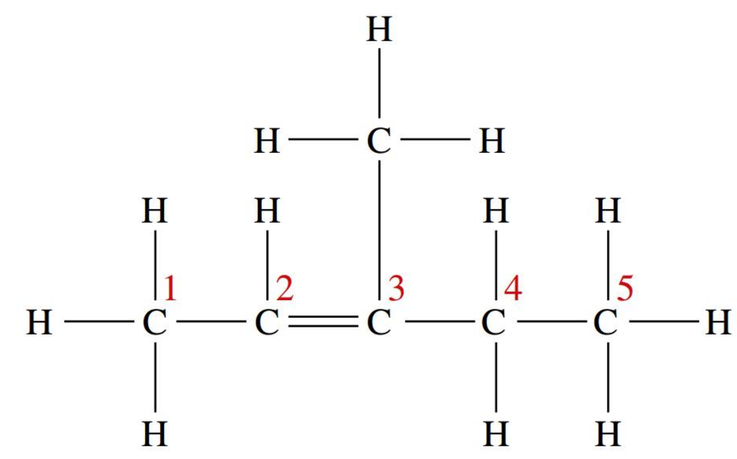
4. If two identical side chains are present, use 'di-' as a prefix; for three, use 'tri-'. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas (not required for this example).
5. If there are alkyl side chains of different lengths on the molecule, list them in alphabetical order at the start of the name. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas (not required for this example).
6. Combine all components to write the full name. Write the name as a single word with hyphens to separate numbers from letters and commas to separate numbers.
   - The name of the molecule is 4-methylpent-2-ene.

Worked example 8.2.3

IUPAC NAMING SYSTEM FOR ALKENES

Analyse the following molecule and determine its systematic name.

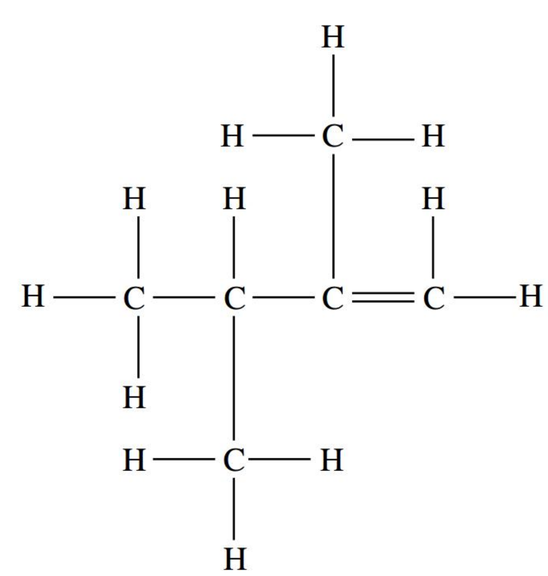


Thinking	Working
Identify the longest continuous carbon chain in the molecule that contains the double bond. The name of the molecule is based on this longest chain.	There are five carbon atoms in the longest chain. The name is based on pentene.
Number the carbon atoms starting from the end closest to the double bond. Note the position of the double bond.	 There is a double bond on carbon number 2, so the longest chain is pent-2-ene (this is the parent name).
Determine the name of each alkyl side chain and identify the carbon atom in the main chain that each is attached to. In this case, there is only one alkyl side chain.	The side chain is a methyl group and it is on carbon number 3. It will therefore be named as 3-methyl.
Combine all components to write the full name. Write the name as a single word with hyphens to separate numbers from letters and commas to separate numbers.	The systematic name of the molecule is 3-methylpent-2-ene.

➤ Try yourself 8.2.3

IUPAC NAMING SYSTEM FOR ALKENES

Analyse the following molecule and determine its systematic name.

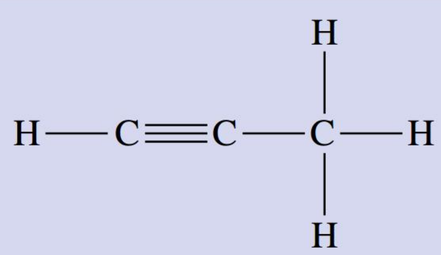
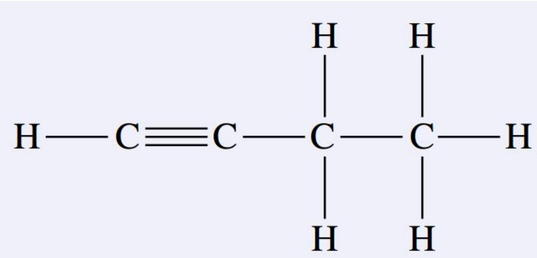


Alkynes

Alkynes are a homologous series of hydrocarbons with one carbon–carbon triple bond. The triple bond is a functional group that gives alkynes their chemical properties; just like the alkenes, alkynes are more reactive than alkanes because of their functional group. The general formula for alkynes with one triple bond is C_nH_{2n-2} and the presence of the triple bond means the alkynes are described as being unsaturated. The shape around each of the carbon atoms in the triple bond is linear.

The formulas and uses of the first three members of the homologous series of alkynes are shown in Table 8.2.5. You can see that successive members differ by a $-CH_2-$ unit and that each alkyne follows the general formula C_nH_{2n-2}, where n represents the number of carbon atoms.

TABLE 8.2.5 Formulas and uses of the first three members of the alkyne homologous series

Name	Molecular formula	Structural formula	Condensed structural formula	Uses
ethyne	C_2H_2		CH≡CH	welding: an oxy-acetylene (ethyne is also known as acetylene) flame has a temperature of about 3000°C
propyne	C_3H_4		$CH{\equiv}CCH_3$	possible rocket fuel
but-1-yne	C_4H_6		$CH{\equiv}CCH_2CH_3$	as a reactant in the synthesis of other organic compounds

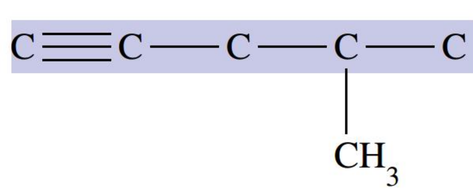
Naming alkynes

Like the alkenes, the rules for naming alkynes follow the same general rules used for alkanes. However, there are a few differences, which are outlined below.

- Use the ending '-yne' as the suffix for the parent name.
- Number the carbon atoms from the end of the chain closest to the triple bond.
- Specify the position of the triple bond by the number of the lowest-numbered carbon atom in the triple bond.
- Insert the number into the name immediately before '-yne'.

The following steps show the process of naming the alkyne shown in Figure 8.2.7.

1. Identify the longest continuous carbon chain that contains the triple bond. The name of the molecule is based on this chain.



- It is a five-carbon chain, so the name of the molecule is based on pentyne.

Alkynes are unsaturated hydrocarbons that contain one carbon–carbon triple bond.

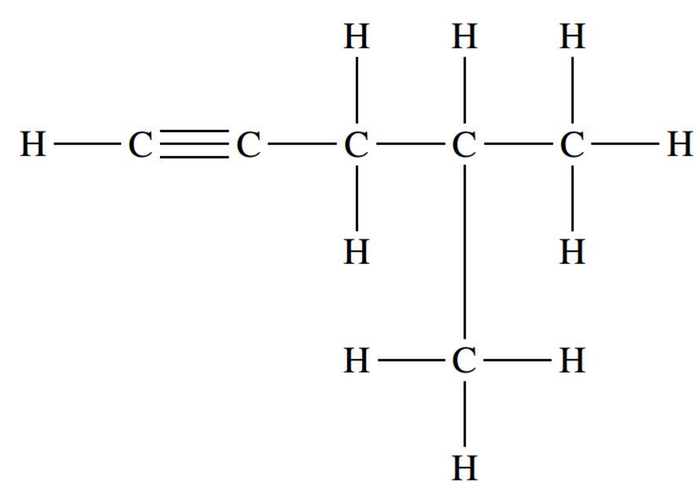
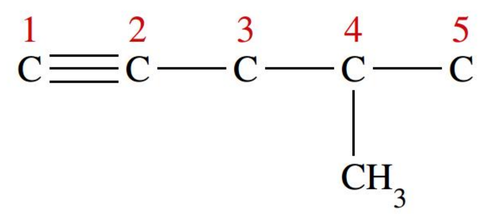


FIGURE 8.2.7 The IUPAC system will be used to name this alkyne.

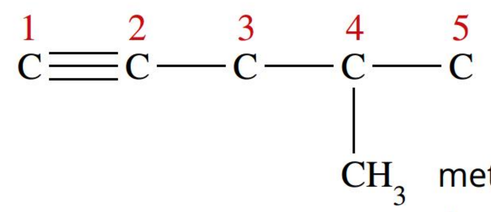
2. Number the carbons, starting from the end closest to the triple bond. Note the position of the triple bond.



five-carbon chain with triple bond on carbon number 1

- It is a five-carbon chain with the triple bond starting at carbon number 1. The parent name is therefore pent-1-yne.

3. Name each alkyl side chain and identify the number of the carbon atom in the main chain that each is attached to.



methyl group on carbon number 4
4-methyl

- There is a methyl group on carbon number 4. It will be named 4-methyl.

4. If two identical side chains are present, use 'di-' as a prefix; for three, use 'tri-'. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas (not required for this example).
5. If there are alkyl side chains of different lengths on the molecule, list them in alphabetical order at the start of the name. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas (not required for this example).
6. Combine all components to write the full name. Write the name as a single word with hyphens to separate numbers from letters and commas to separate numbers.
   - The name of the molecule is 4-methylpent-1-yne.

IUPAC rules for omitting numbers

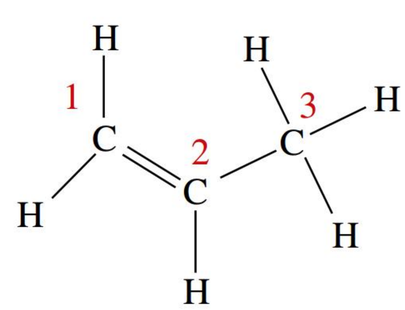
Although it is common practice to omit numbers whenever a structure is unambiguous (e.g. propene, rather than prop-1-ene), the IUPAC rules are not as general as this. A **locant** (number indicating the location of a multiple bond) may only be omitted in specified situations. For the molecules studied in this course:

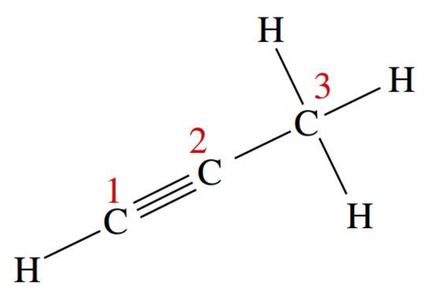
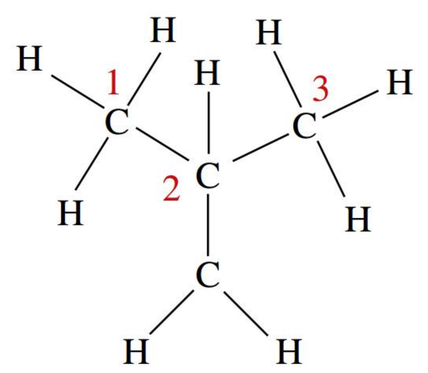
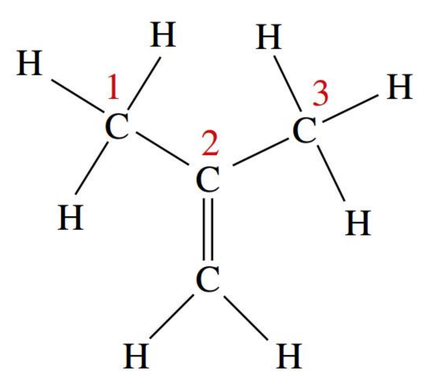
- A locant can only be omitted if the multiple bond is located on the first carbon **and** the location in the molecule is unambiguous (i.e. there is only one possible location for the multiple bond.)
- If one locant is needed, then all locants should be specified for that molecule.

For example, the locant is omitted in propene and propyne.

In contrast, locants are required in 2-methylpropane and 2-methylprop-1-ene even though these structures are unambiguous without locants.

You may find these molecules commonly referred to as methylpropane and methylpropene, but these are not the correct systematic IUPAC names.

Structural formula	Correct IUPAC systematic name
	propene (no locant needed as the only possible position for the C=C is on the first carbon)

	propyne (no locant needed as the only possible position for the carbon–carbon triple bond is on the first carbon)
	2-methylpropane (locant required by IUPAC rules as the methyl group is on the second carbon, even though the name is unambiguous without the locant)
	2-methylprop-1-ene (as one locant is needed (2-methyl), all others must also be given)

8.2 Review

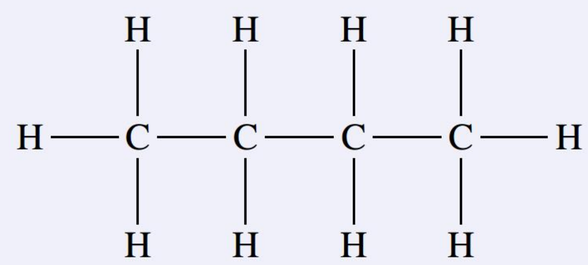
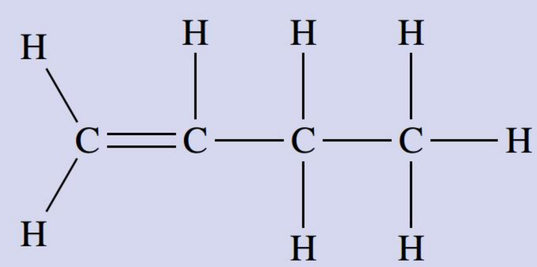
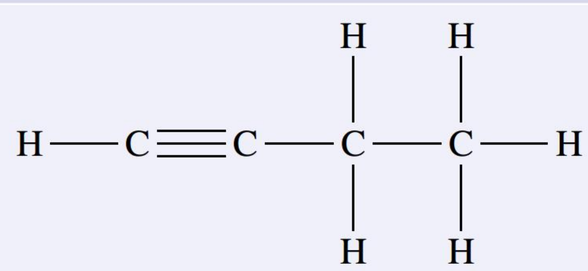
SUMMARY

- Hydrocarbons are compounds containing carbon and hydrogen only.
- In a homologous series, each member has one more $–CH_2–$ unit than the previous member. Members of a homologous series have similar structures and chemical properties and have the same general formula.
- Alkanes are the simplest hydrocarbons. They are saturated hydrocarbon molecules because they only contain single covalent bonds.
- Alkanes have the general formula C_nH_{2n+2}.
- Alkanes have a tetrahedral shape around each carbon atom.
- Unsaturated hydrocarbons are hydrocarbons that contain one carbon–carbon double or triple bond.
- Alkenes are a homologous series of hydrocarbons that contain a carbon–carbon double bond.
- Alkenes have the general formula C_nH_{2n}.
- Alkenes have a trigonal planar shape around each carbon atom in the double bond.
- Alkynes are a homologous series of hydrocarbons that contain a carbon–carbon triple bond.
- Alkynes have the general formula C_nH_{2n-2}.
- Alkynes have a linear shape around each carbon atom in the triple bond.
- Table 8.2.6 provides a summary of the main classes of hydrocarbons and the functional groups that each class contains.
- The IUPAC naming system is used to provide systematic names for hydrocarbon molecules. The following conventions are used for naming hydrocarbons.

Continued over page

8.2 Review *continued*

TABLE 8.2.6 A summary of the main classes of hydrocarbons

Class	General formula	Functional group	Example
alkanes	C_nH_{2n+2}	none	 butane
alkenes	C_nH_{2n}	carbon–carbon double bond	 but-1-ene
alkynes	C_nH_{2n-2}	carbon–carbon triple bond	 but-1-yne

- There are no spaces in a name.
- The longest carbon chain is used to derive the parent name. The longest chain must include the double or triple bond for alkenes and alkynes.
- Suffixes are used in the parent name to indicate whether the hydrocarbon is an alkane, alkene or alkyne; '-ane' is used for alkanes, '-ene' for alkenes and '-yne' for alkynes.
- Numbers are used in the parent name to identify carbon atoms that contain double or triple bonds. The names and locations of alkyl side chains are added to this parent name.
- If there is more than one type of alkyl side chain to be listed at the beginning of a name, they are listed in alphabetical order.
- If there is more than one of the same type of alkyl side chain, the prefixes 'di-' or 'tri-' are used.
- Numbers and letters are separated by dashes.
- Numbers are separated from other numbers by commas.

KEY QUESTIONS

Describe

1 State the general formula for:
- **a** an alkane
- **b** an alkene
- **c** an alkyne.

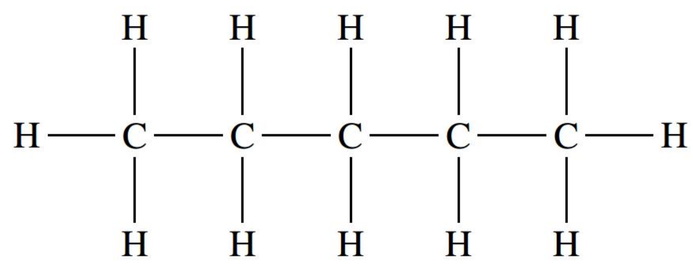
2 Define the following terms.
- **a** alkane
- **b** alkene
- **c** alkyne

3 The molecular formulas for three hydrocarbons are given below. Identify whether each is an alkane, an alkene or an alkyne.
- **a** C_4H_8
- **b** C_6H_{14}
- **c** C_2H_2

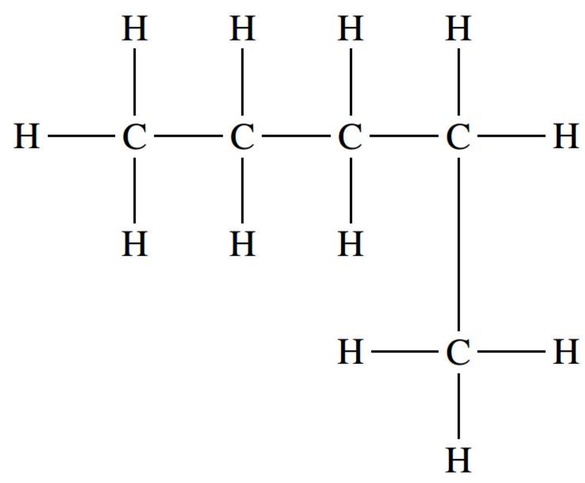
Apply

4 Use the systematic naming rules to determine the names of the following alkanes.

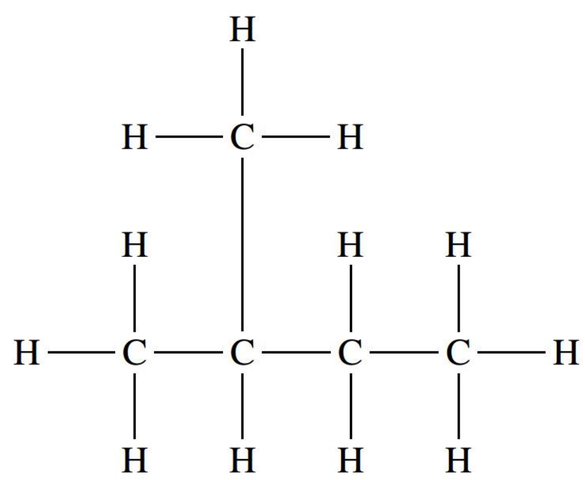
a



b



c



5 The following relates to the hydrocarbon with the molecular formula C_3H_8.

- **a** Draw the extended structural formula of this hydrocarbon.
- **b** Determine the name of this hydrocarbon.
- **c** Represent the hydrocarbon with its condensed structural formula.

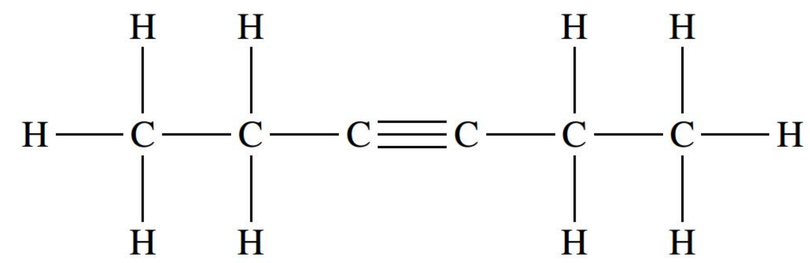
Analyse

6 Categorise the following alkenes in order from lowest to highest number of carbon atoms:

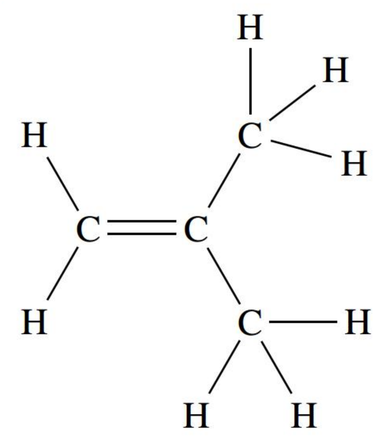
pent-1-ene, ethene, non-1-ene, oct-1-ene, propene

7 Determine the systematic names of the unsaturated hydrocarbons shown below.

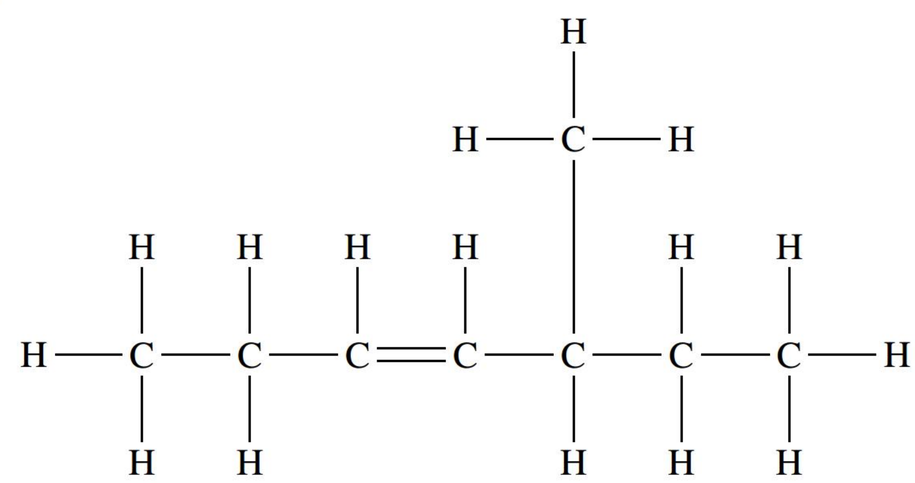
a



b



c



8 Analyse the names of the following alkanes. Show the extended structural formula and determine the condensed structural formula for each one.

- **a** 2,4-dimethylpentane
- **b** 2,2-dimethylhexane
- **c** 4-ethyl-2-methylhexane

9 Analyse the following alkane names. Determine why they are incorrect and provide the correct name.

- **a** 3-methylbutane
- **b** 2-ethylpropane
- **c** 1-methylpentane

10 Analyse the names of the following unsaturated hydrocarbons. Show the extended structural formula and determine the condensed structural formula for each one.

- **a** 2,3-dimethylpent-2-ene
- **b** 2,2-dimethyloct-3-yne
- **c** 3-ethyl-2-methylhex-1-ene

8.3 Isomerism

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- define isomers and know that the two main types are structural isomers and stereoisomers
- know that isomers can have different properties
- define structural isomers and know that they can be formed by changing the position of any functional groups and/or by varying the chain length while keeping the molecular formula the same
- identify structural isomers from structural formulas (either extended or condensed)
- represent structural isomers when given either the molecular formula or the structural formula of another isomer
- define stereoisomers and know that the two main types are geometrical isomers and optical isomers
- define geometric isomers and know that they are also called *cis-trans* isomers
- understand that geometrical isomers can occur when there is restricted rotation of bonds in a molecule, as occurs when there is a carbon–carbon double bond
- identify molecules in which *cis-trans* isomers are possible
- represent structural formulas for *cis-trans* isomers
- understand that optical isomers are non-superimposable mirror images of each other
- understand that optical isomers can occur when a molecule contains a chiral carbon atom
- identify a chiral carbon in an organic molecule
- apply systematic naming rules to name structural and geometric isomers.

Isomers have the same molecular formula, but the atoms are arranged differently.

Isomers are molecules that contain the same number and type of atoms, arranged in different ways. The existence of isomers is a major reason why there are so many different carbon compounds. Isomers have the same **molecular formula**, but they can have different physical and chemical properties, and so behave differently.

There are two main types of isomers:

- structural isomers
- stereoisomers.

STRUCTURAL ISOMERS

Structural isomers form when the atoms in molecules with the same molecular formula bond together in different arrangements. To identify the structural isomers possible, it can be useful to think about two ways in which the molecule can be changed: by changing the chain length and/or by changing the position of any functional groups.

Isomers formed by changing the chain length

Because branching is possible in the carbon chains that form the backbone of any large organic molecule, isomers with differing main chain lengths can be formed. These isomers of **alkanes** (the simplest hydrocarbons) can contain more than one

alkyl group (a branch or side chain formed from an alkane); some molecules may also have more than one alkyl group attached to the same carbon atom.

Hexane is an example of an alkane with no branches. It has the molecular formula C_6H_{14} and its structure is shown in Figure 8.3.1.

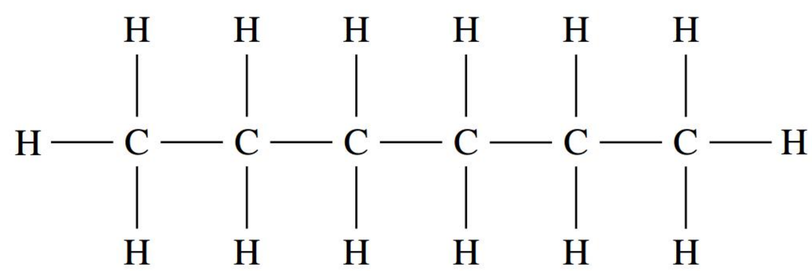


FIGURE 8.3.1 Hexane is a single-chain hydrocarbon with single bonds that contains 6 carbon atoms and 14 hydrogen atoms.

Three of the isomers of hexane that can be formed by changing the main chain length are shown in Figure 8.3.2. Each isomer has a different name that represents its exact molecular structure. The naming of these isomers is described in the next section.

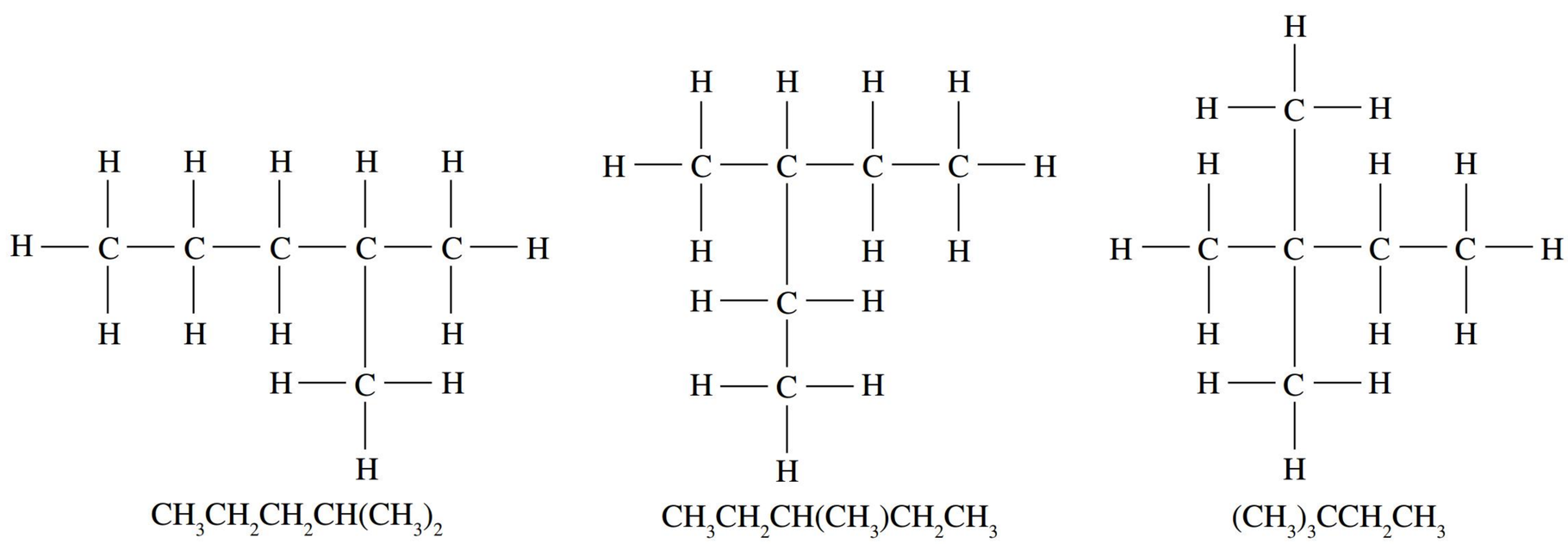


FIGURE 8.3.2 Three isomers of hexane

Isomers formed by changing the position of functional groups

Structural isomers can also occur for organic molecules that contain functional groups. Molecules with the same carbon chain and functional group can form isomers when the functional group is attached to a different location in the molecule.

For example, **alcohols** are organic molecules that contain a **hydroxyl functional group** (–OH). Several isomers can be drawn for an alcohol with the molecular formula $C_4H_{10}O$. Again, each isomer is distinguished by being given a different name. Figure 8.3.3 shows two isomers, butan-1-ol and butan-2-ol.

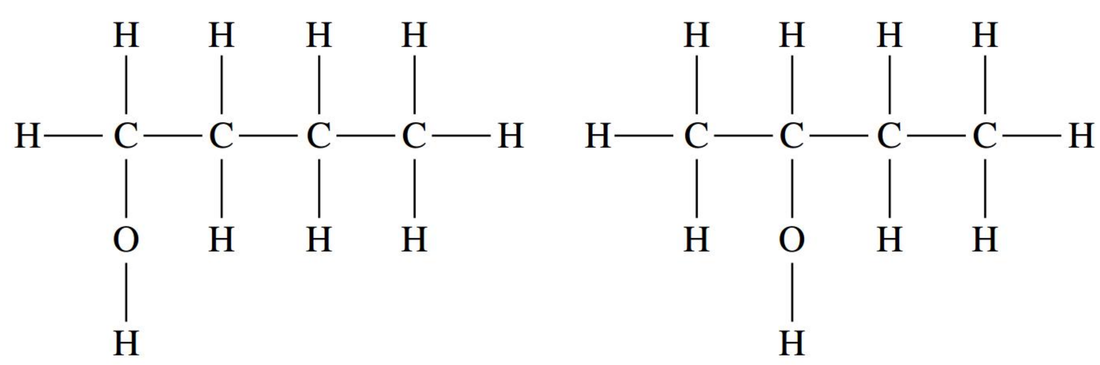


FIGURE 8.3.3 Two isomers of $C_4H_{10}O$

It is important to realise that alkenes also contain a functional group—their double carbon–carbon bond. This means that structural isomers can be formed when the double bond is in different locations. Figure 8.3.4 shows the two isomers of butene.

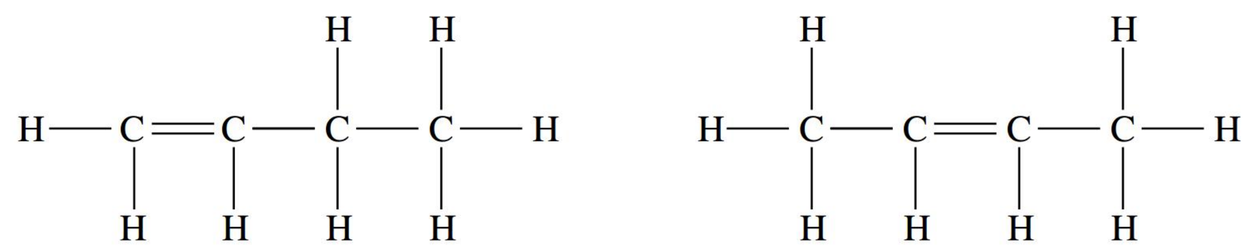


FIGURE 8.3.4 The two isomers of butene: but-1-ene and but-2-ene

When drawing structural isomers, be careful that you do not just draw the same molecule from a different perspective. You can see that the two structural formulas of ethanol in Figure 8.3.5 do not represent isomers.

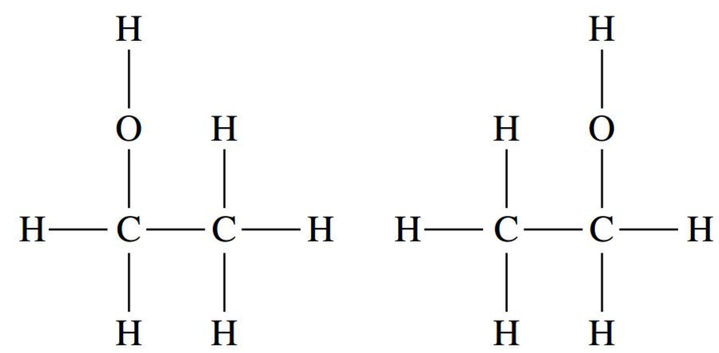


FIGURE 8.3.5 Two representations of the structure of ethanol (C_2H_6O). These are not isomers; if the first structure is flipped over, it is identical to the second.

It is possible for molecules to form isomers by changing both the length of the chain and the position of a functional group. Figure 8.3.6 shows two more isomers of an alcohol with the formula $C_4H_{10}O$. For these isomers to form, both the length of the main chain and the position of the functional group have been changed.

> **i** Structural isomers can be formed by changing the length of the main chain and/or the position of functional groups.

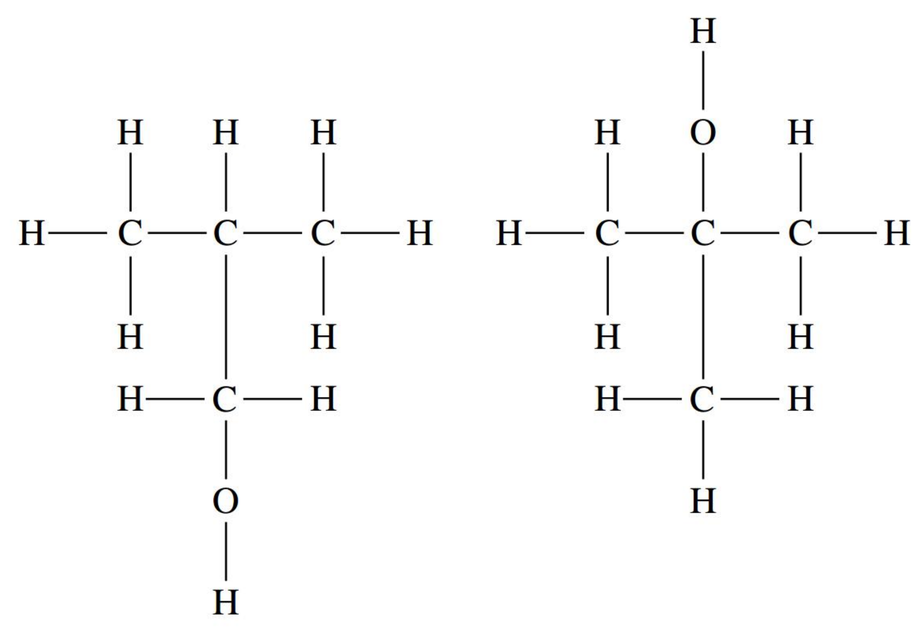
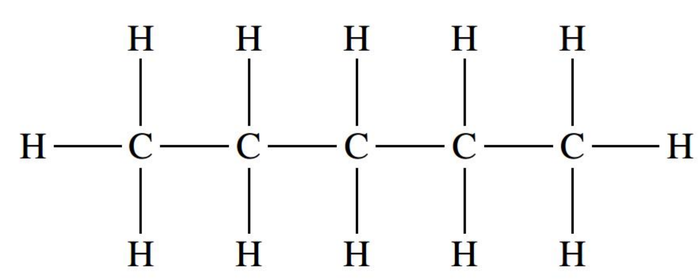


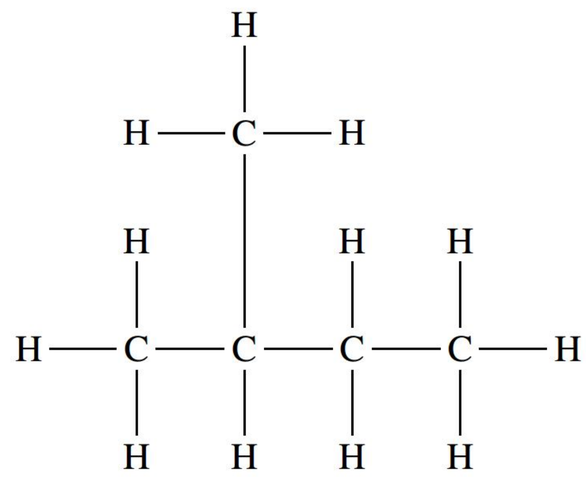
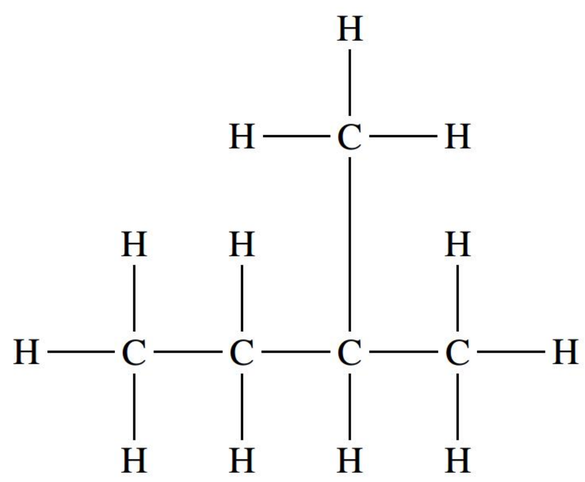
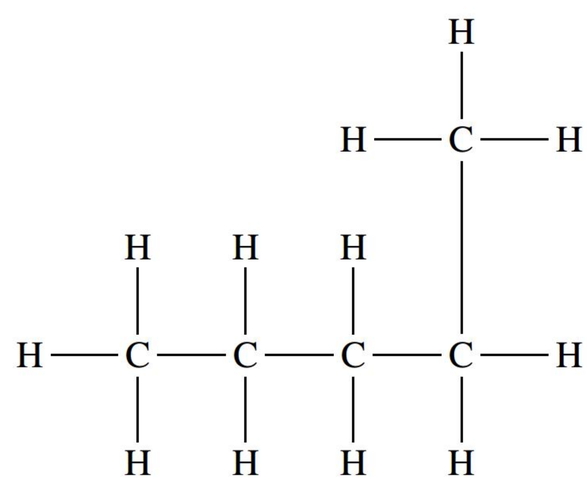
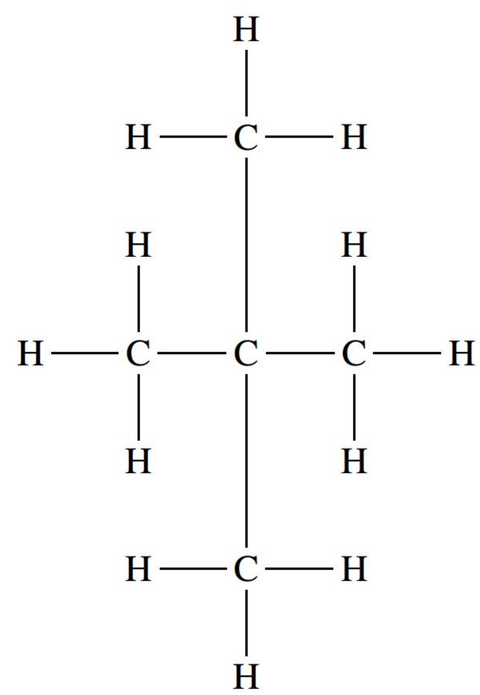
FIGURE 8.3.6 Two more molecules that are alcohols with the molecular formula $C_4H_{10}O$

Worked example 8.3.1

DRAWING STRUCTURAL ISOMERS

Determine the structural formulas for the three alkanes with the molecular formula C_5H_{12}.

Thinking	Working
Alkanes do not contain a functional group, so the structural isomers will be formed by changing the chain length. Identify the straight-chain molecule; draw and name it. This is the first alkane.	There are five carbon atoms in the chain. The name of this alkane is 'pentane'.  pentane

Determine the structural formula of the second alkane by drawing the main chain again, but this time with one less carbon atom. The parent alkane will now have four carbon atoms and will be based on a butane molecule. Next, add a methyl group to as many positions in the main chain as possible, so that you obtain different structures. Name the structures.	The methyl group can be added to carbon number 2 to make 2-methylbutane. This is the only structural isomer possible based on a butane molecule.  2-methylbutane
It is important to name each of the structures you draw to ensure that you do not draw the same molecule twice.	These structures below might seem different because you have added the methyl group to carbon numbers 3 and 4 in the chain, respectively. However, when you name them, you can see that they are actually the molecules pentane and 2-methylbutane, which you have already drawn. Therefore, these are NOT new isomers.  2-methylbutane  pentane
Represent the structural formula of the third alkane by drawing the main chain with one less carbon again. The parent alkane will now have three carbon atoms and will be based on a propane molecule. Next, add two methyl groups to as many positions in the main chain as possible, so that you obtain different structures. Name the structures.	The two methyl groups can be added to carbon number 2 to make 2,2-dimethylpropane. There are no more structural isomers possible based on the propane molecule.  2,2-dimethylpropane

➤ Try yourself 8.3.1

DRAWING STRUCTURAL ISOMERS

Determine the structural formulas for the three structural isomers of the alkene with the molecular formula C_4H_8.

Stereoisomers are isomers in which the atoms in two molecules are connected in the same order but have different arrangements in space. Stereoisomers can have very different chemical and physical properties.

STEREOISOMERS

Stereoisomers are isomers in which the atoms are connected in the same order but have different arrangements in space. Stereoisomers differ in their three-dimensional shape, so the name of this type of isomer begins with the stem 'stereo-' (meaning 'three dimensional'). Two types of stereoisomers are optical isomers and geometric (*cis-trans*) isomers, and they can be formed by a range of organic molecules.

Optical isomers

Optical isomers are a type of stereoisomer where there is different placement of groups around one atom in a molecule. The molecules have exactly the same molecular and condensed structural formulas.

These isomers are called optical isomers because they were first noticed by the different ways they interact with plane-polarised light. Plane-polarised light contains waves that oscillate in a single plane.

When plane-polarised light shines through some organic molecules, its plane of polarisation is rotated. Different substances rotate the light to different extents and in different directions (clockwise or anticlockwise). A pair of optical isomers rotate plane-polarised light by the same amount but in opposite directions (Figure 8.3.7).

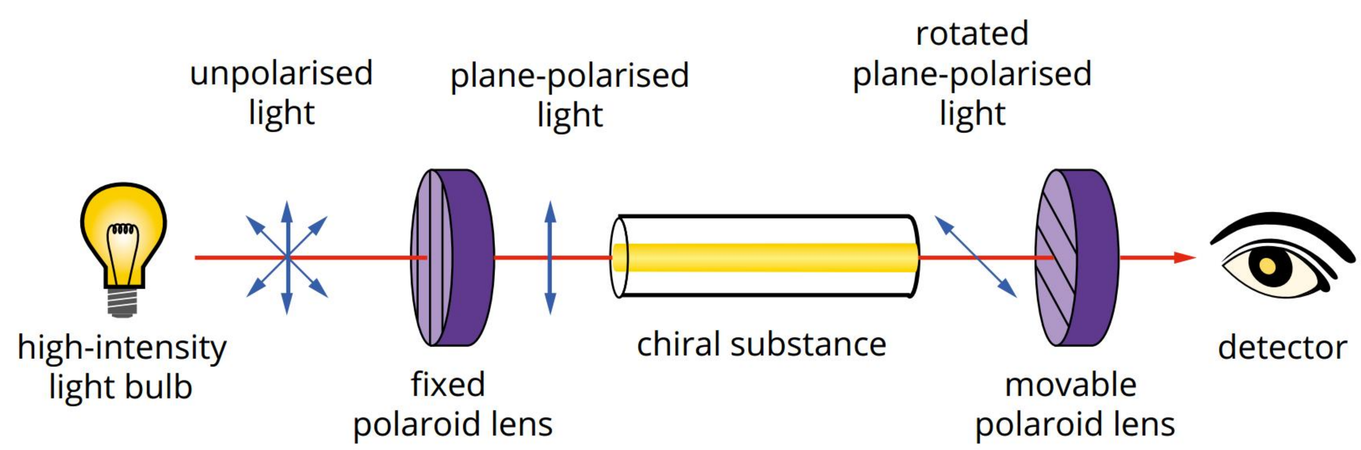


FIGURE 8.3.7 Some organic substances rotate plane-polarised light. The angle and direction of the rotation between the fixed and movable polaroid lenses allow the different optical isomers to be identified.

Chirality

An object is **chiral** if it has a non-superimposable mirror image.

Substances that can form optical isomers are known to be **chiral**. Two objects are chiral when they are mirror images of each other, and the mirror images cannot be superimposed on top of each other.

The term 'chiral' comes from the Greek word for hand. Your hands are chiral objects. One hand is a mirror image of the other, yet a left and right hand cannot be superimposed, one on top of the other. It is even simpler to think about your feet. Again, your left and right feet are mirror images but cannot be superimposed. Your left shoe does not fit on your right foot, as shown in Figure 8.3.8.

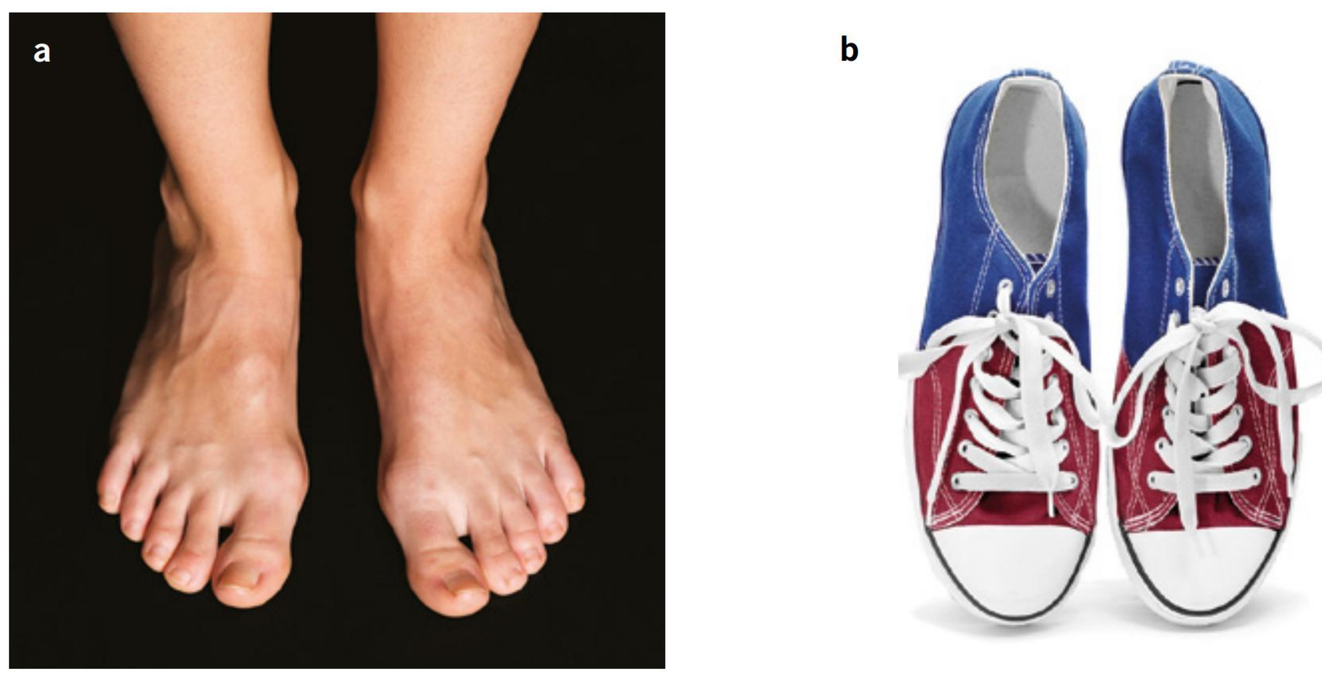


FIGURE 8.3.8 Your feet are chiral. They are mirror images but cannot be superimposed or fit in the same three-dimensional space, meaning that a right foot does not fit in a left shoe.

Other examples of chiral objects are shown in Figure 8.3.9.

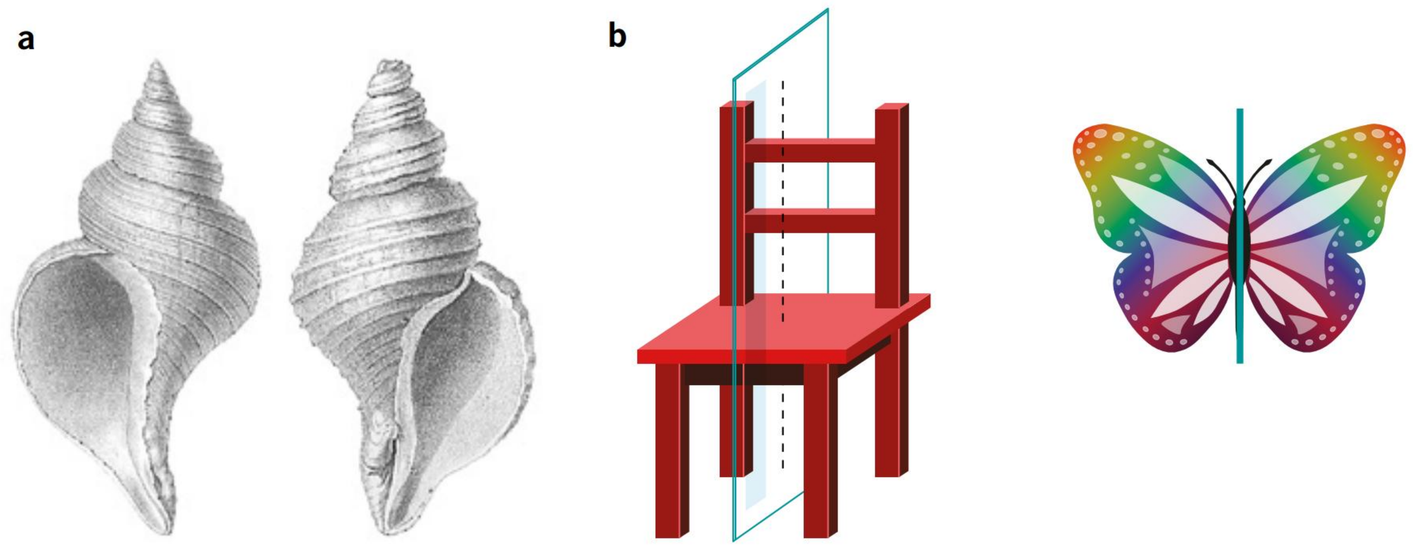


FIGURE 8.3.9 (a) These shells are chiral. The shell on the right is the mirror image of the shell on the left. It cannot be superimposed on the left-hand shell. (b) This chair and butterfly each have a plane of symmetry. The left side is exactly the same as the right. This means the chair and the butterfly are achiral.

Achiral objects (objects that are not chiral) are objects whose mirror images can be superimposed on the original. Chiral objects lack a **plane of symmetry**, whereas objects that are achiral have at least one plane of symmetry. A plane of symmetry exists when a three-dimensional figure can be divided into two halves that are mirror images. You can see some examples in Figure 8.3.10.

Chirality in organic molecules

Organic molecules that are chiral include molecules with a carbon atom joined to four different groups in a tetrahedral arrangement. A pair of chiral molecules are called **enantiomers**.

Chiral molecules come in pairs, called **enantiomers.**

In Figure 8.3.10, you can see that molecule A is a mirror image of molecule B. The mirror image cannot be superimposed on the first molecule as the arrangement of the four groups in space is different. When molecule A is rotated so that the red and green groups are in the same position as in molecule B, the purple and yellow groups are in different places. The two molecules are chiral.

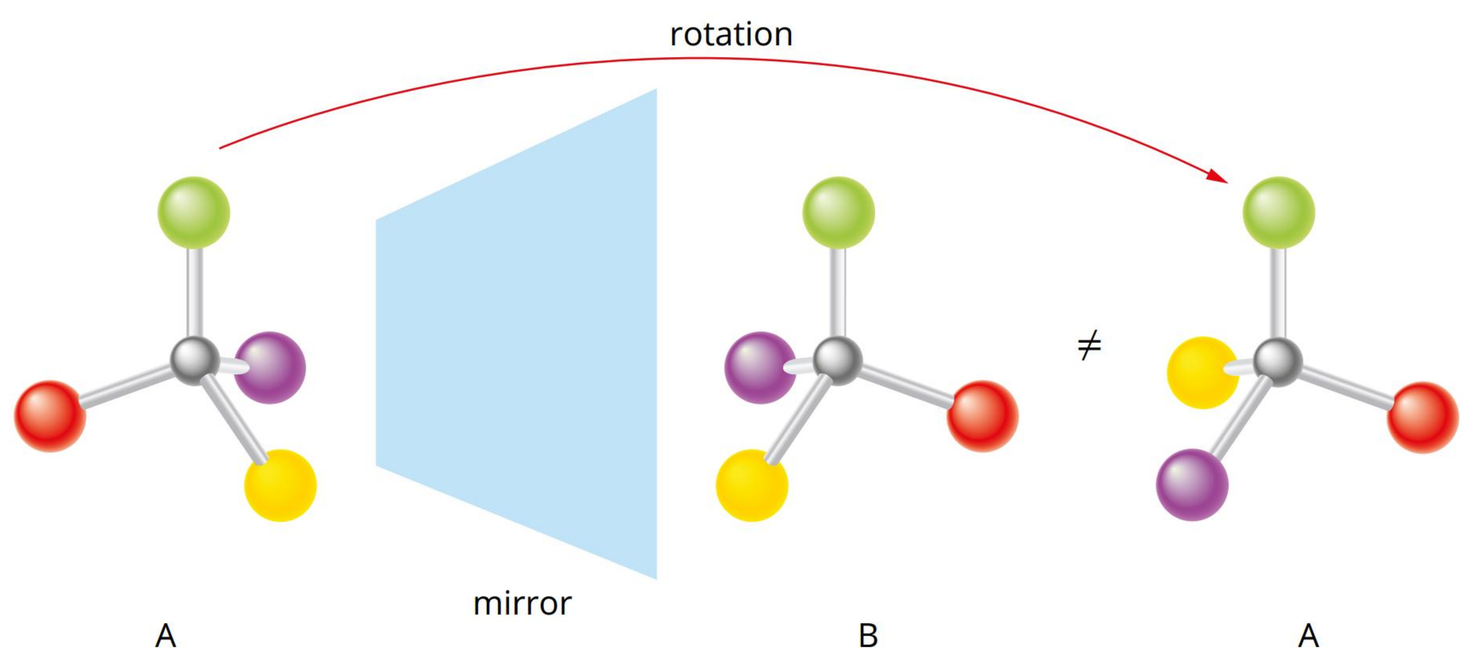


FIGURE 8.3.10 The molecules A and B represented by these ball and stick models are a pair of enantiomers.

A carbon atom attached to four different groups is called a **chiral centre**. A chiral molecule must contain at least one chiral centre. A chiral molecule must contain no planes of symmetry overall.

A chiral centre can be identified by looking at the four groups attached to a carbon atom. If the carbon atom is attached to four different groups, then it is a chiral centre, and the molecule may have optical isomers.

The molecule in Figure 8.3.11 is chiral and a pair of enantiomers is shown. The carbon in the centre is attached to four different groups, which makes it the chiral centre. Often the chiral centre is marked with an asterisk. The bonds from the carbon to the hydrogen and chlorine are shown as simple lines to show that these are flat against the page. The wedged line represents a bond coming out of the page

and the dashed wedge represents a bond going into the page. A rotated view of enantiomer A is shown with the hydrogen and chlorine atoms in the same position as enantiomer B. This results in the bromine and fluorine atoms being in different places and shows that the mirror image is not the same.

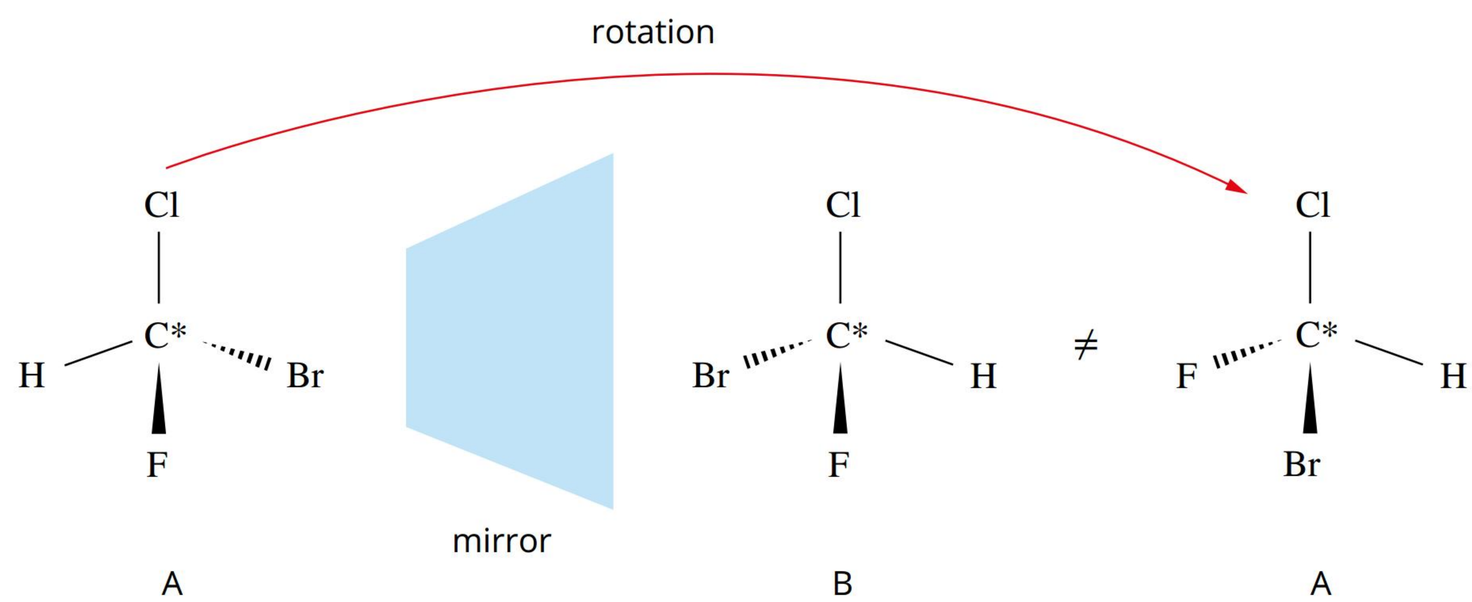


FIGURE 8.3.11 Bromochlorofluoromethane is a chiral molecule and has two enantiomers.

The molecule in Figure 8.3.12 does not contain a chiral centre because there are two identical groups bonded to the carbon atom. It is an achiral molecule. The mirror image of the molecule can be rotated to produce a structure that can be superimposed on the original. They are the same molecule and are not enantiomers.

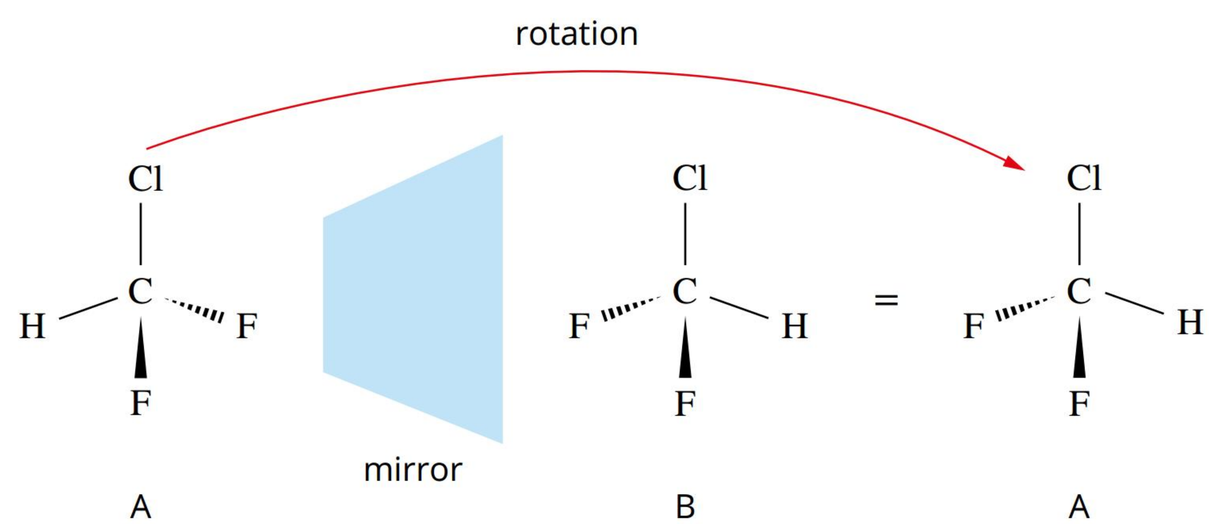


FIGURE 8.3.12 Chlorodifluoromethane is an achiral molecule because its mirror image can be superimposed.

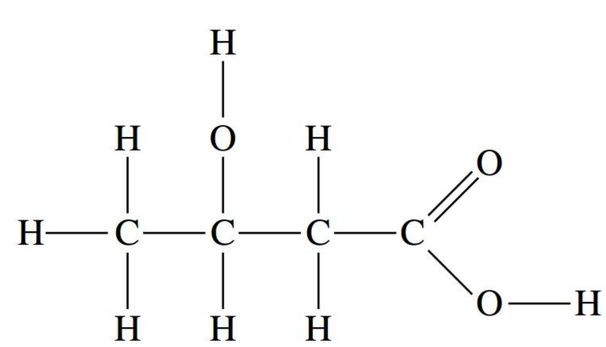
Identifying chiral centres

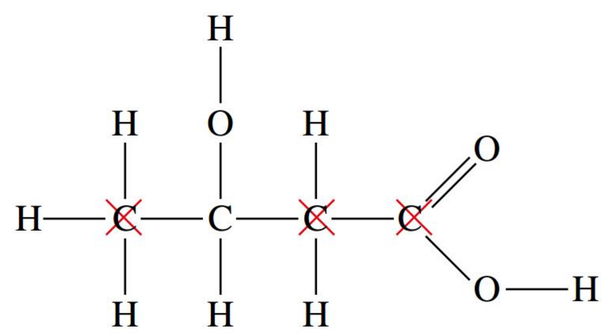
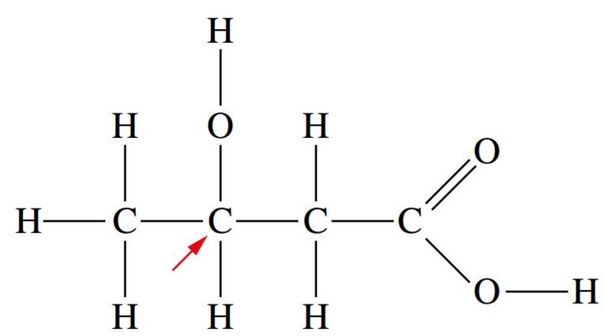
To identify a chiral centre, you need to determine if any of the carbon atoms in a molecule has four different groups attached. As Worked example 8.3.2 illustrates, you often need to look further than just the next atom to see if the groups are the same.

Worked example 8.3.2

IDENTIFYING CHIRAL CENTRES IN ORGANIC MOLECULES

Identify any chiral centres in the following molecule.

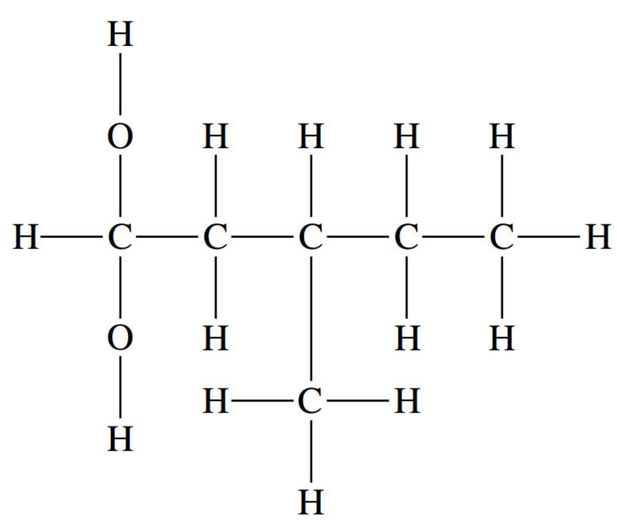


Thinking	Working
Eliminate the carbon atoms that cannot be chiral centres. This includes all $-CH_3$ and $-CH_2-$ groups and any atom that is part of a double or triple bond, because these carbon atoms cannot be bonded to four different groups.	 This leaves one carbon atom that may or may not be a chiral centre.
For each remaining carbon atom, examine the groups attached to the atom. If there are four different groups, the atom is a chiral centre.	 The remaining carbon atom has the following groups attached: $-CH_3$ $-H$ $-OH$ $-CH_2COOH$ The four groups are different, so this carbon atom is a chiral centre.

➤ Try yourself 8.3.2

IDENTIFYING CHIRAL CENTRES IN ORGANIC MOLECULES

Identify any chiral centres in the following molecule.



Properties of enantiomers

Enantiomers have identical physical properties, apart from the way they rotate plane-polarised light. For example, they have the same melting and boiling points and the same solubility in water.

However, enantiomers usually interact differently with other chiral molecules. The human body contains mainly chiral molecules, so molecules that are chiral have different effects on the body. Figure 8.3.13 shows the example of the compound carvone. One enantiomer of carvone has the odour of spearmint, whereas the other enantiomer has the odour of caraway seeds. Many pharmaceutical drugs exist as enantiomers, with only one enantiomer having a beneficial effect on the body.

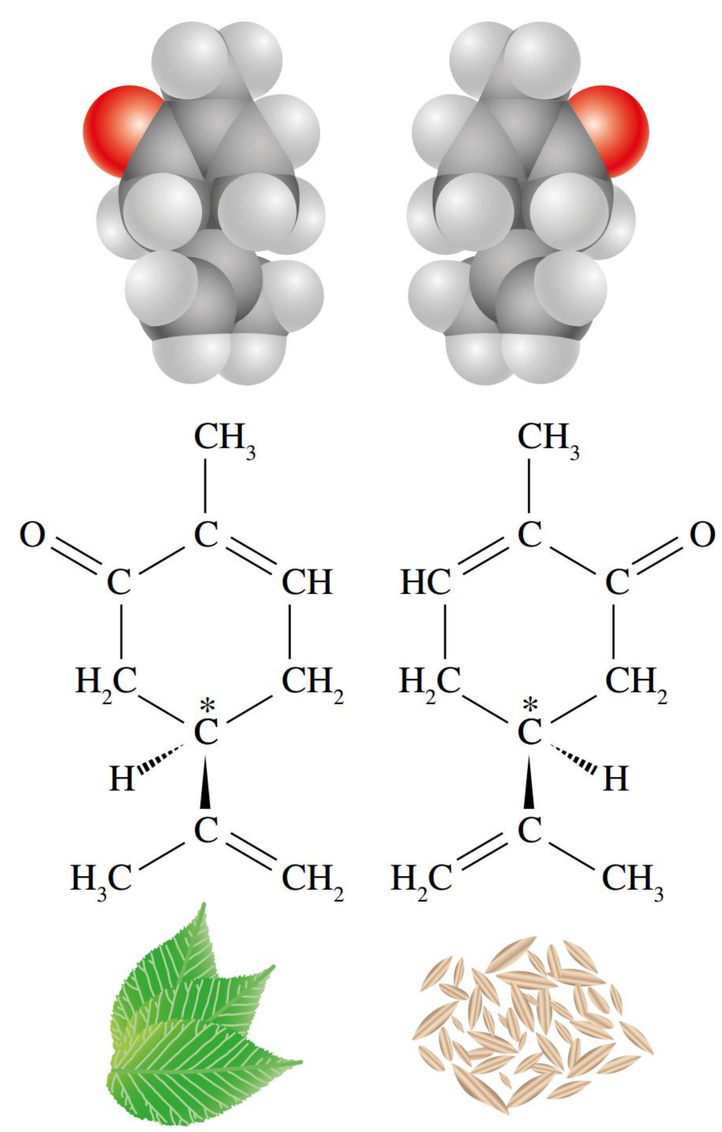


FIGURE 8.3.13 Carvone is a chiral molecule with two enantiomers. The enantiomer on the left has the odour of spearmint. The enantiomer on the right has the odour of caraway seeds.

Geometrical isomers are a type of stereoisomer; they are also called *cis*-trans isomers and can occur when atoms are prevented from rotating around a bond, such as a carbon–carbon double bond in an alkene.

Geometric isomers

Geometric isomers are also called ***cis-trans* isomers** and can occur when there is restricted rotation somewhere in a molecule, for example about a carbon–carbon double bond.

Cis-trans isomers of alkenes occur because the atoms associated with the carbon–carbon double bond are fixed in position.

Two atoms joined by a single bond can rotate freely around the single bond. You might think that the two models shown in Figure 8.3.14 show different molecules, but they are representations of the same molecule because there is free rotation around the single bond. The first structure can rotate around the central single bond to look exactly the same as the second.

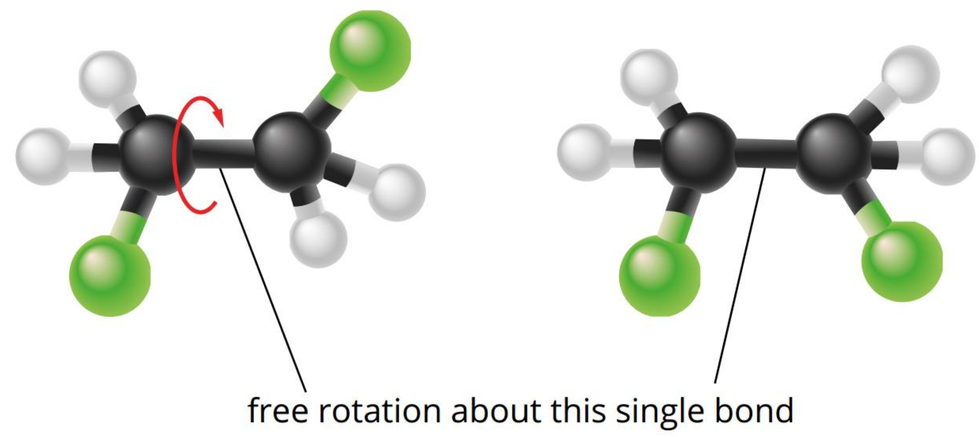


FIGURE 8.3.14 These two models represent the same molecule because the groups on either end can rotate around the single bond.

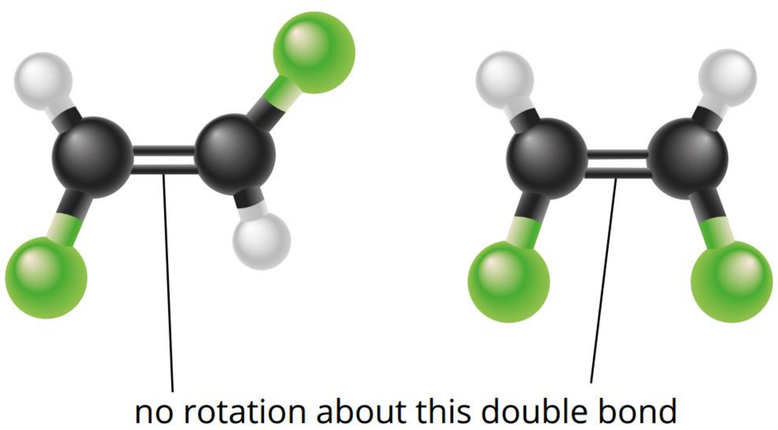


FIGURE 8.3.15 These two models represent different molecules because the groups on either end cannot rotate around the double bond.

However, because of the way that the electrons are arranged in a double bond, groups attached to the carbons on either side of the double bond are unable to rotate freely. The models in Figure 8.3.15 represent two molecules that cannot be rotated to form the same structure because a carbon–carbon double bond is present.

Cis-trans isomers only occur when each carbon atom in the double bond is attached to two different groups, as shown in Figure 8.3.16 (if even just one of the carbon atoms in the double bond is attached to two groups that are identical, then *cis-trans* isomerism cannot occur).

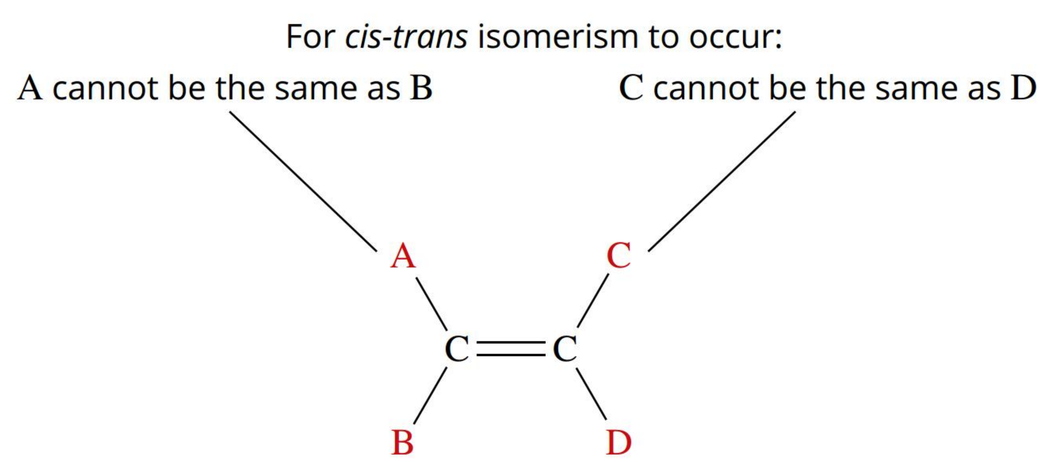


FIGURE 8.3.16 For *cis-trans* isomerism to occur, each carbon atom in the double bond must be attached to two different groups.

The different groups can be hydrogen atoms, functional groups or hydrocarbon chains of different lengths. There are two possible arrangements: the functional groups or hydrocarbon chains can be on the same side or opposite sides of the double bond. If they are on the same side, the isomer is called the ***cis*-isomer**. If they are on opposite sides, the isomer is called the ***trans*-isomer**.

Figure 8.3.17 shows the three possible structures of dibromoethene ($C_2H_2Br_2$). If both bromine atoms are attached to the first carbon atom, then it is called 1,1-dibromoethene. This molecule does not have geometric isomers because the two groups attached to each carbon atom in the double bond are identical. If the bromine atoms are attached to different carbon atoms, then it is called 1,2-dibromoethene, and has the condensed structural formula BrCH=CHBr. There are two geometric isomers possible: *cis*-1,2-dibromoethene and *trans*-1,2-dibromoethene.

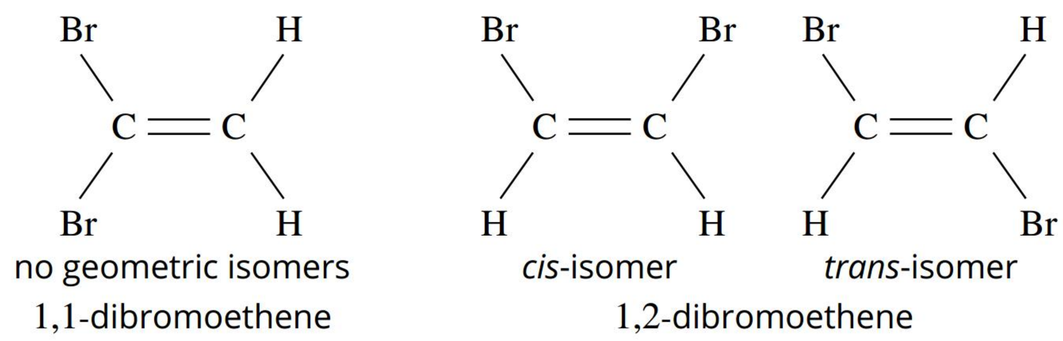


FIGURE 8.3.17 The possible structures of dibromoethene ($C_2H_2Br_2$). Note the position of the bromine atoms in the *cis*- and *trans*-isomers.

When considering longer alkenes, it is the longest alkyl groups attached to the carbon atoms in the double bond that are used to decide if the molecule is a *cis*- or *trans*-isomer.

- In *cis*-isomers, the longest alkyl groups on each carbon are located on the same side of the double bond.
- In *trans*-isomers, the longest alkyl groups on each carbon are located on opposite sides of the double bond.

Figure 8.3.18 shows the *cis*- and *trans*-isomers of but-2-ene. The two methyl groups are on the same side of the double bond in the *cis*-isomer. The methyl groups are opposite to each other in the *trans*-isomer.

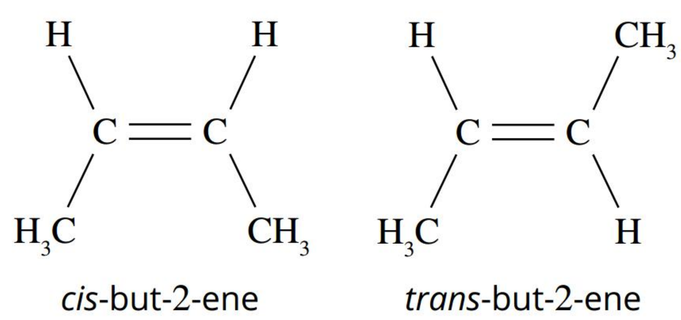
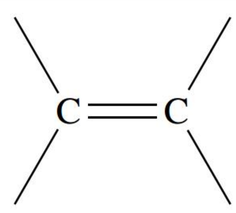
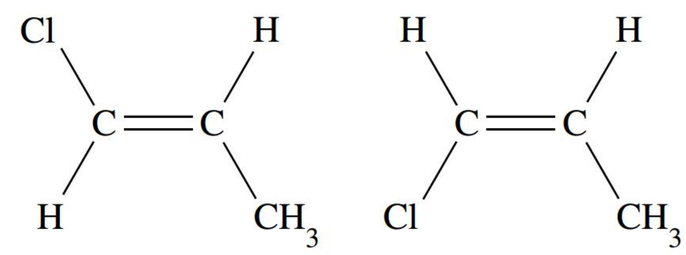


FIGURE 8.3.18 The two geometric isomers of but-2-ene

Worked example 8.3.3

DRAWING GEOMETRIC ISOMERS

Determine the *cis*- and *trans*-isomers of 1-chloroprop-1-ene.	
Thinking	**Working**
State the condensed structural formula of the molecule.	$ClHC{=}CHCH_3$
Draw the structural formula of the carbon skeleton around the double bond showing the trigonal planar shape.	
Analyse the condensed structural formula to identify the groups that are attached to each side of the double bond.	There is a hydrogen atom and a chlorine atom attached to the left-hand carbon in the double bond. There is a hydrogen atom and a methyl (CH_3) group attached to the right-hand carbon in the double bond.

In the *trans*-isomer, the chlorine and methyl groups will be located on opposite sides of the double bond. In the *cis*-isomer, the chlorine and methyl groups will be located on the same side of the double bond.	 *trans*-isomer *cis*-isomer

➤ Try yourself 8.3.3

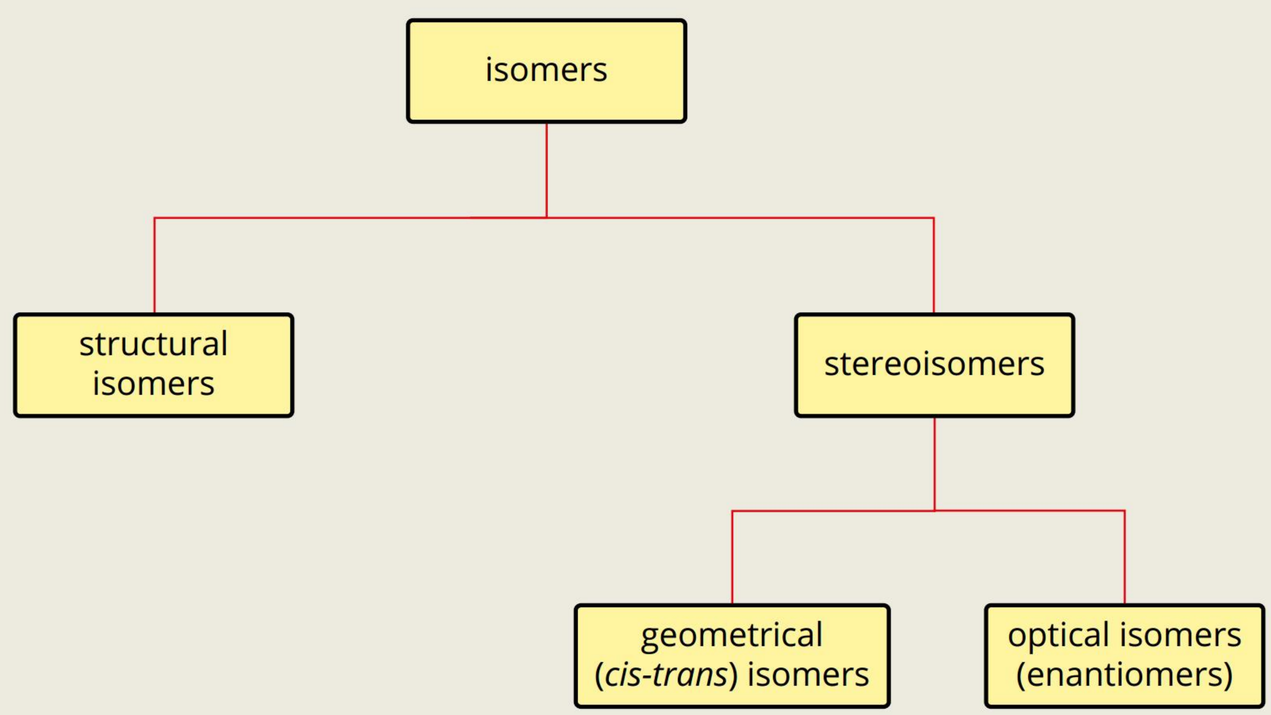
DRAWING GEOMETRIC ISOMERS

Determine the *cis*- and *trans*-isomers of pent-2-ene.

8.3 Review

SUMMARY

- Isomers are molecules that have the same molecular formula but their atoms are arranged in different ways.
- Structural isomers are molecules that have the same molecular formula but a different connectivity of atoms (i.e. they have a different structure).
- Stereoisomers are molecules that have the same molecular formula, the same connectivity of atoms, but a different arrangement of those atoms in space. Two types of stereoisomers are optical isomers and geometrical (*cis* and *trans*) isomers.
- Optical isomers are stereoisomers that can occur when a molecule is chiral. An object is chiral if it cannot be superimposed on its mirror image.
- Chiral molecules come in pairs, called enantiomers.
- Optical isomers can form when a chiral carbon is present in a molecule.
- A chiral carbon can be identified when a carbon atom is bonded to four different groups.
- Geometrical (*cis* and *trans*) isomers are stereoisomers that can occur where there is restricted rotation somewhere in a molecule. Restricted rotation can occur about a carbon–carbon double bond.
- Geometrical (*cis and trans)* isomerism can occur in alkenes when there are two different groups attached to each carbon atom involved in the double bond.
- In *cis*-isomers, the substituent (non-hydrogen) groups are attached to the same side of the double bond.
- In *trans*-isomers, the substituent groups are attached to the opposite sides of the double bond.
- The chart gives a summary of the different types of isomers. Isomers can be classified into two main groups: structural isomers and stereoisomers.



KEY QUESTIONS

Describe

1 Define the term 'isomer'.

2 Describe the feature that must be present in a molecule for geometrical isomers to be possible.

3 Name the feature that must be present in a molecule for optical isomers to be possible.

4 Identify the prefixes given to the two geometrical isomers that can form.

5 State the name given to a pair of optical isomers.

Apply

6 Explain the difference between structural isomers and stereoisomers.

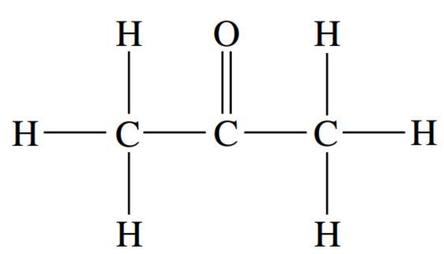
7 Explain why geometrical (*cis* and *trans*) isomers occur in alkenes but not in alkanes.

8 Explain how a chiral centre can be identified.

Analyse

9 Analyse the following molecules and identify the number of chiral centres.

a



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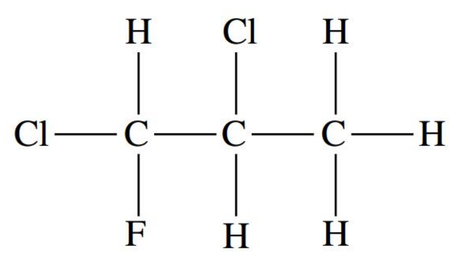
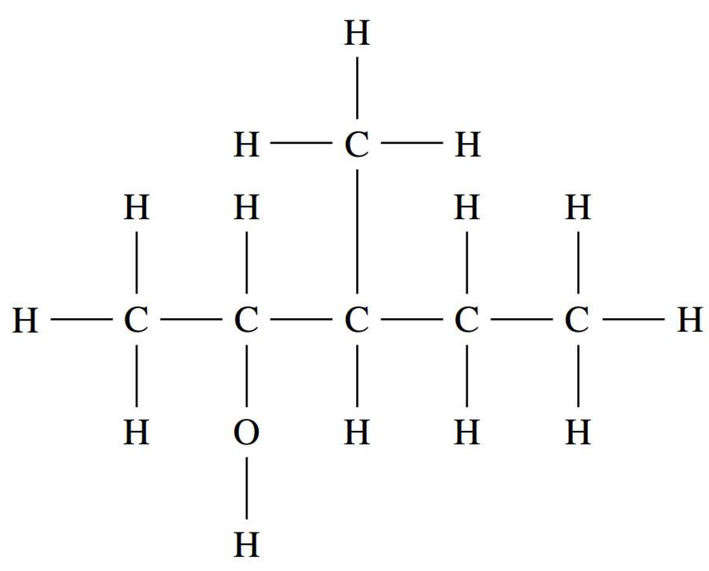
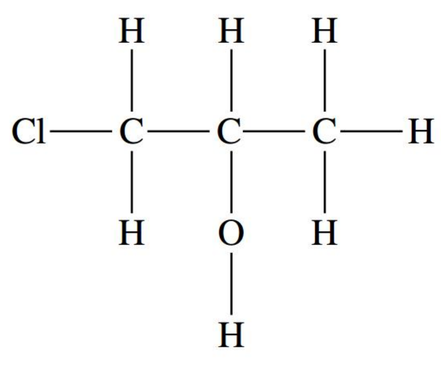


c



d



10 There are four structural isomers with the molecular formula $C_3H_6Br_2$. Determine the structural formulas for these isomers.

11 Determine and name the five structural isomers of the alkanes with the molecular formula C_6H_{14}.

12 Analyse the following condensed structural formulas of two different organic compounds.

$H_2C{=}CHCH_3$ — propene

$H_3CHC{=}CHBr$ — 1-bromoprop-1-ene

a Determine which molecule shows *cis-trans* isomerism.

b Draw the *cis*- and *trans*-isomers for this molecule.

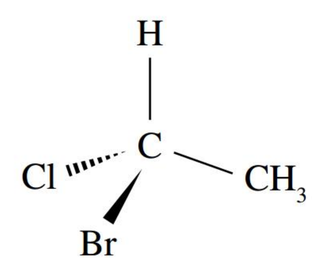
c Explain why the other molecule cannot show *cis-trans* isomerism.

13 Determine why the name *cis*-hex-1-ene is incorrect.

14 **a** Determine the smallest chain length that any organic molecule could have and still show *cis-trans* isomerism.

b Determine the smallest chain length that a hydrocarbon molecule could have and still show *cis-trans* isomerism.

15 Draw the enantiomer of the following molecule and show that it is a non-superimposable mirror image of this molecule:



16 From the following list of compounds, determine whether each could have optical isomers, geometrical isomers, both types of stereoisomer or neither type of stereoisomer.

a 1,2-dibromoethene

b 1,1-dibromoethene

c bromodichloromethane

d bromochlorofluoromethane

8.4 Hydrocarbon derivatives

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- recall that organic compounds are organised into classes or homologous series based on their functional groups
- identify the functional groups present in alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides
- deduce the structural formulas and apply IUPAC rules in the nomenclature of organic compounds with simple branching for alcohols, aldehydes, ketones, carboxylic acids and esters, up to C10
- identify a primary, secondary or tertiary carbon atom in a haloalkane or alcohol.

In Module 8.2, you studied the three classes of hydrocarbons, namely the alkanes, alkenes and alkynes, and learnt that the carbon-to-carbon double bond in alkenes and the carbon-to-carbon triple bond in alkynes can be considered to be functional groups because they are responsible for the properties of the compounds in each class.

However, as discussed in Module 8.1, there are organic compounds that are not hydrocarbons as they contain other elements in addition to carbon and hydrogen. These compounds are known as hydrocarbon derivatives. Hydrocarbon derivatives have a hydrocarbon skeleton but contain functional groups in which one or more of the hydrogen atoms in the hydrocarbon skeleton have been replaced with other atoms or groups of atoms.

In this module, you will examine the functional groups that make up each class of the hydrocarbon derivatives and use systematic naming rules to name some of the compounds in these classes.

FUNCTIONAL GROUPS AND CLASSES OF HYDROCARBON DERIVATIVES

The presence of a particular functional group in a molecule gives a substance certain physical and chemical properties. For example, vinegar and wine both contain organic molecules based on ethane. The difference between their tastes and other properties is due to the different functional groups in each molecule. Vinegar contains ethanoic acid, which has a carboxyl functional group, and wine contains ethanol, which has a hydroxyl functional group. This can be seen in Figure 8.4.1.

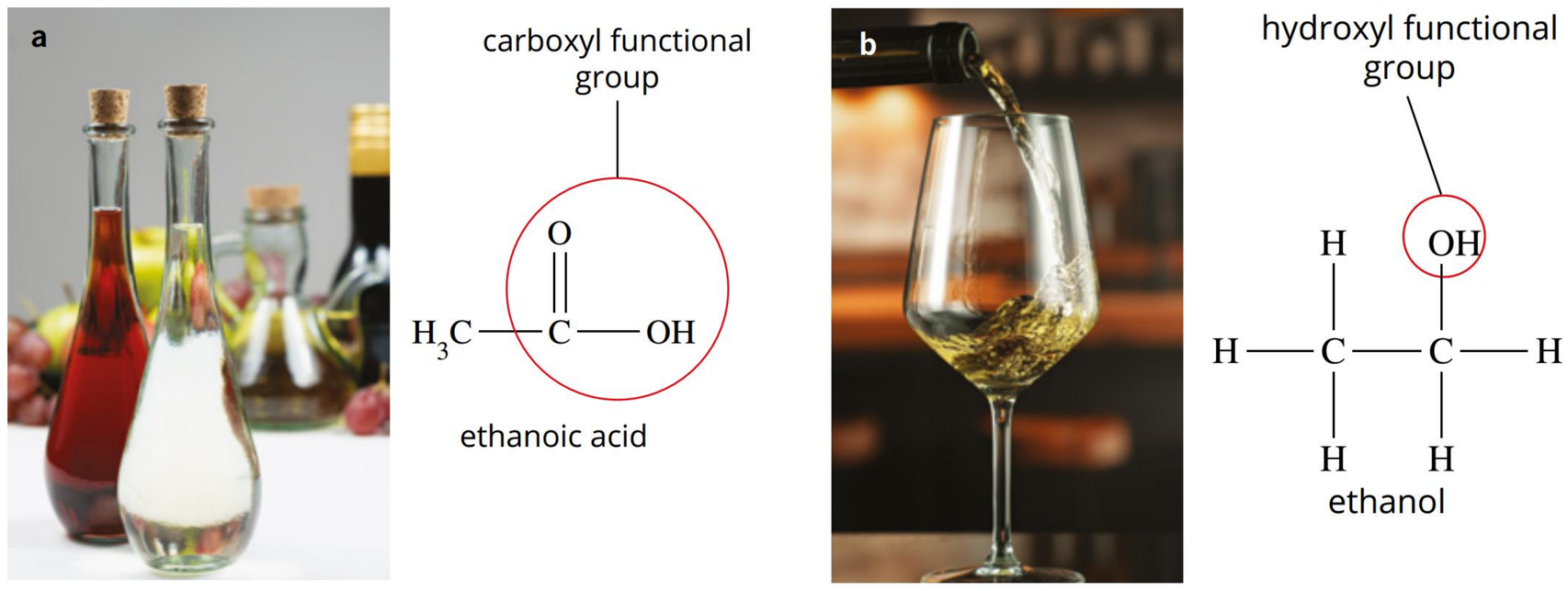
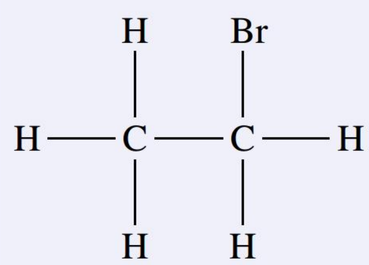
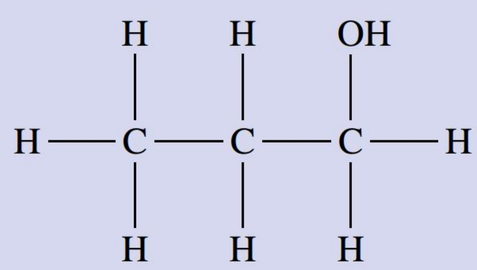
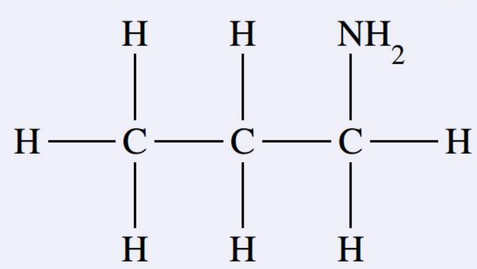
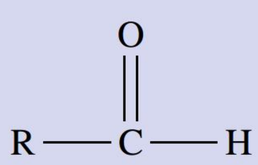
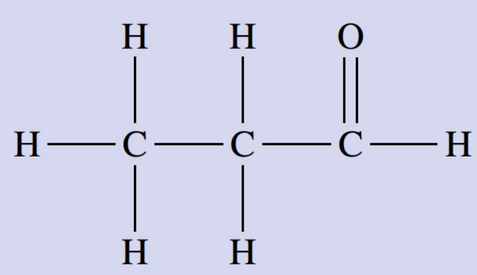
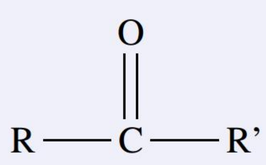
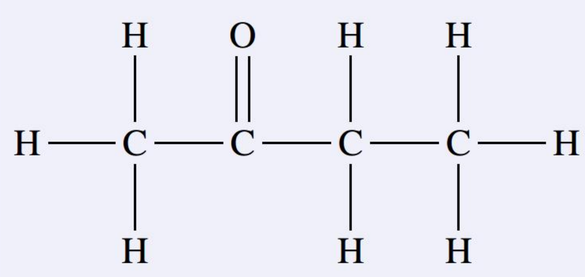
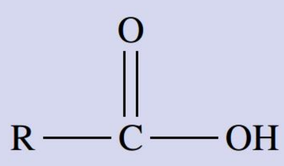
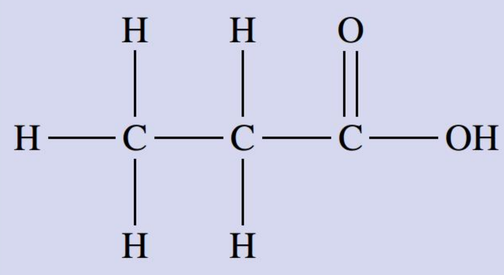


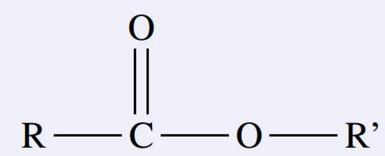
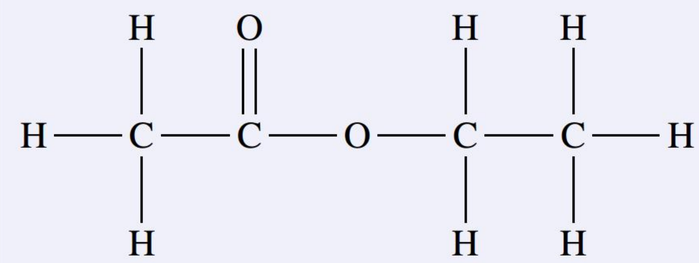
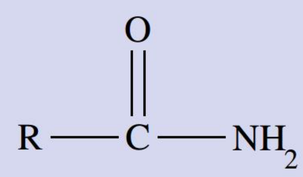
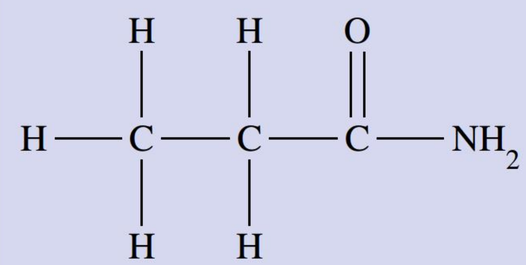
FIGURE 8.4.1 (a) Vinegar and (b) wine contain molecules with two carbon atoms. Vinegar contains ethanoic acid with a carboxyl functional group and wine contains ethanol with a hydroxyl group.

We can organise the millions of known organic compounds into classes or homologous series based on their functional groups; this makes it easier for us to understand the chemistry of many different compounds.

The different classes of hydrocarbon derivatives and the functional groups that make up each class are summarised in Table 8.4.1. Remember that the symbols R and R' usually represent the hydrocarbon chain that makes up the rest of the organic molecule, but they can also be used to represent any group of atoms.

TABLE 8.4.1 The different classes of hydrocarbon derivatives and the functional groups that make up each class

Class of hydrocarbon derivative	Functional group present	Example
haloalkane	halogen R–X (where X = F, Cl, Br, I)	bromoethane 
alcohol	hydroxyl R–OH	propan-1-ol 
amine	amino R–NH_2	propan-1-amine (note: naming of amines is not required for this course.) 
aldehyde	carbonyl (attached to a hydrogen atom) 	propanal 
ketone	carbonyl (attached to carbon atoms on either side) 	butan-2-one 
carboxylic acid	carboxyl 	propanoic acid 

Class of hydrocarbon derivative	Functional group present	Example
ester	ester 	ethyl ethanoate 
amide	amide 	propanamide (note: naming of amides is not required for this course.) 

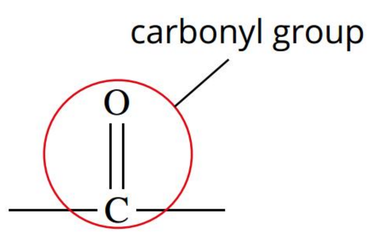


FIGURE 8.4.2 The carbonyl group contains a carbon atom doubly bonded to an oxygen atom. It is found in five of the nine classes of hydrocarbon derivatives covered in this course.

The **carbonyl functional group**, shown in Figure 8.4.2, is a common group of atoms found in five of the nine classes of hydrocarbon derivatives. The carbonyl group is made up of a carbon atom doubly bonded to an oxygen atom and is present in **aldehydes**, **ketones**, **carboxylic acids**, **esters** and **amides**.

We will examine the different classes of hydrocarbon derivatives in two sections. The first part will focus on those hydrocarbon derivatives that do not contain the carbonyl group, and the second part will focus on those hydrocarbon derivatives that do contain the carbonyl group.

HYDROCARBON DERIVATIVES WITHOUT THE CARBONYL GROUP

There are four classes of compounds that you should be familiar with that do not contain a carbonyl group. As shown in Figure 8.4.3, these are the **haloalkanes**, **alcohols and amines**.

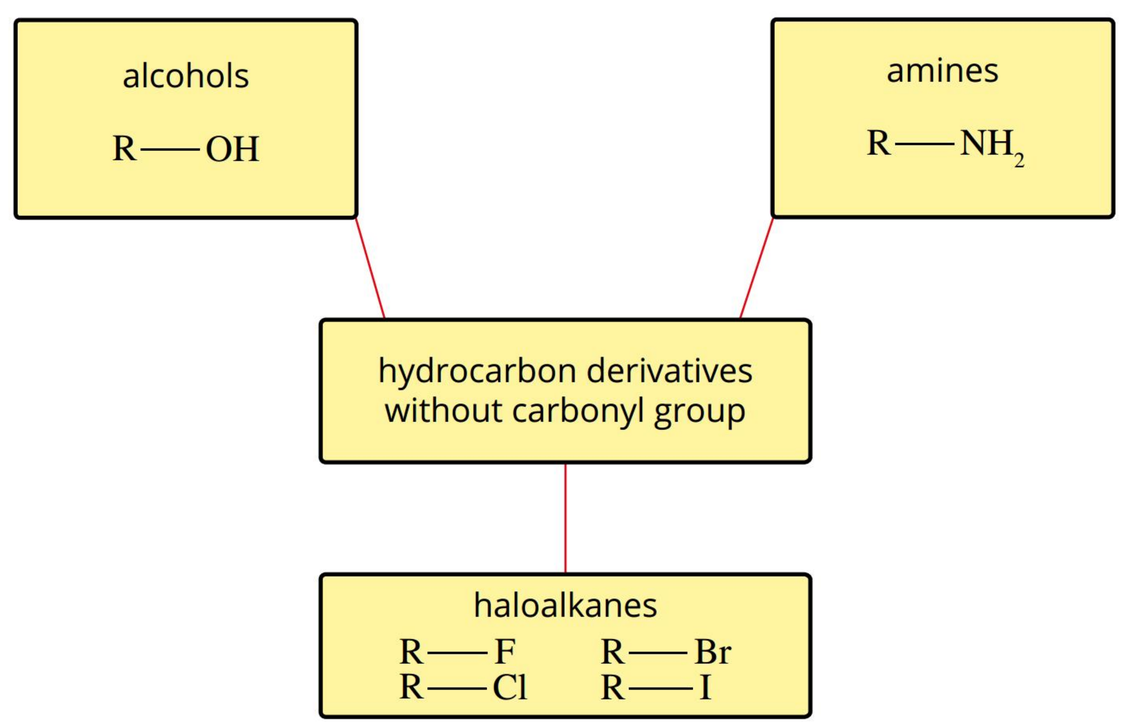


FIGURE 8.4.3 The four classes of hydrocarbon derivatives that do not contain a carbonyl group

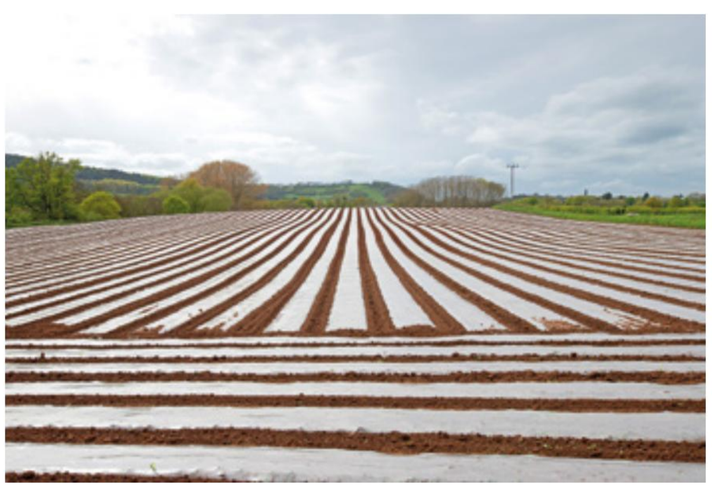


FIGURE 8.4.4 Bromomethane (CH_3Br) is a colourless, odourless, non-flammable gas that was used as a pesticide in the past. This photo shows a field covered in plastic sheeting to minimise loss of the pesticide from the soil. Bromomethane is no longer used as a pesticide as it depletes the ozone layer.

Haloalkanes

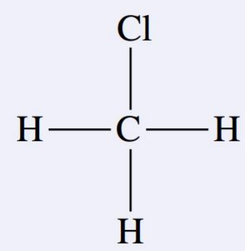
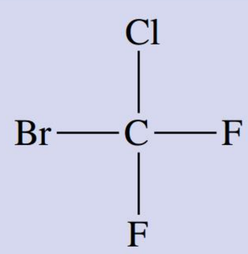
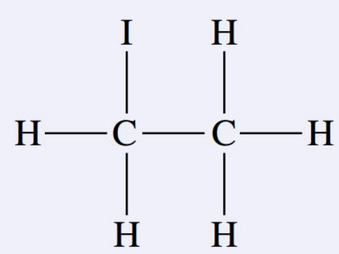
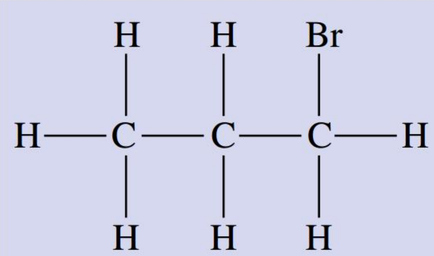
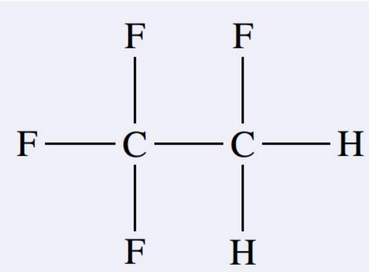
Haloalkanes are a homologous series derived from alkanes in which at least one of the hydrogen atoms is replaced with a **halogen** atom.

Haloalkanes are used widely in industry as flame retardants, refrigerants, propellants, pesticides (Figure 8.4.4), solvents and pharmaceuticals. Some

haloalkanes are ozone-depleting chemicals and their use has been phased out in many applications.

The halogen elements are in group 17 of the periodic table. All halogen atoms have seven valence electrons, which means they can form a single covalent bond with carbon atoms. The halogen elements that commonly form **halo functional groups** in organic compounds are fluorine, chlorine, bromine and iodine. Table 8.4.2 includes the names, structures and uses of some haloalkanes.

TABLE 8.4.2 Names, structures and uses of some haloalkanes

Name	Extended structural formula	Condensed structural formula	Use
chloromethane		CH_3Cl	refrigerant
bromochlorodifluoromethane		$CBrClF_2$	fire extinguishers
iodoethane		CH_3CH_2I	production of chemicals
1-bromopropane		$CH_3CH_2CH_2Br$	industrial solvent
1,1,1,2-tetrafluoroethane		CH_2FCF_3	refrigerant

Classifying haloalkanes

Haloalkanes are classified according to the number of alkyl groups attached to the carbon bonded to the halogen atom. The three different types of haloalkanes are:

- **primary haloalkanes**
- **secondary haloalkanes**
- **tertiary haloalkanes.**

The definition of each type and examples are shown in Table 8.4.3. Alkyl groups are represented by the general symbols R, R' and R".

Haloalkanes are a class of organic compound derived from alkanes in which at least one of the hydrogen atoms is replaced with a halogen atom.

TABLE 8.4.3 The three different types of haloalkanes. The halogen group is shown in red.

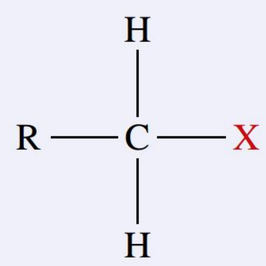
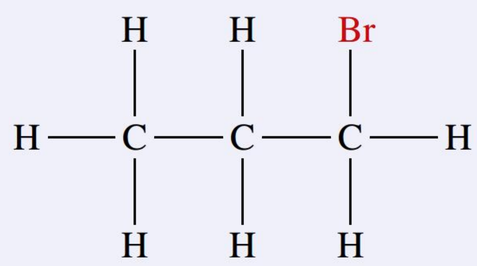
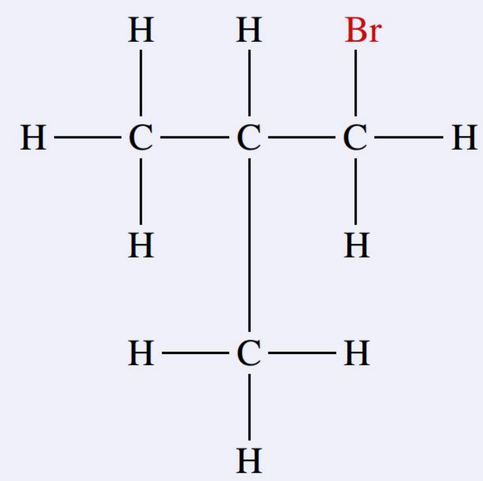
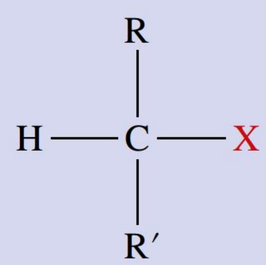
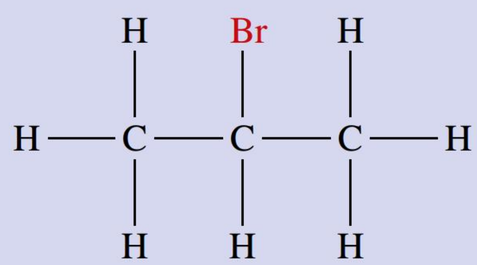
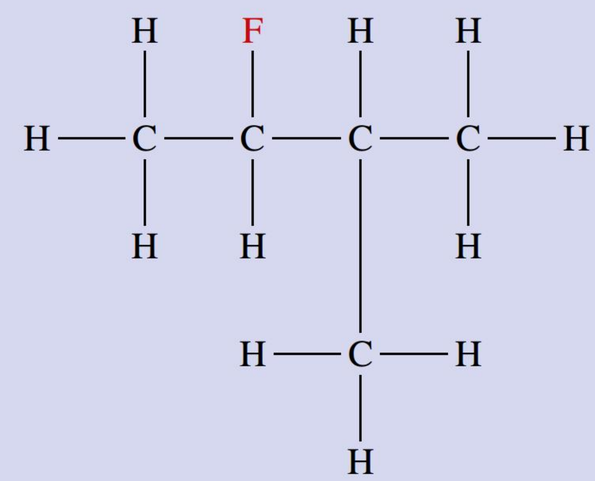
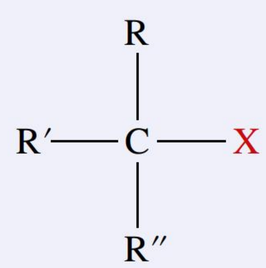
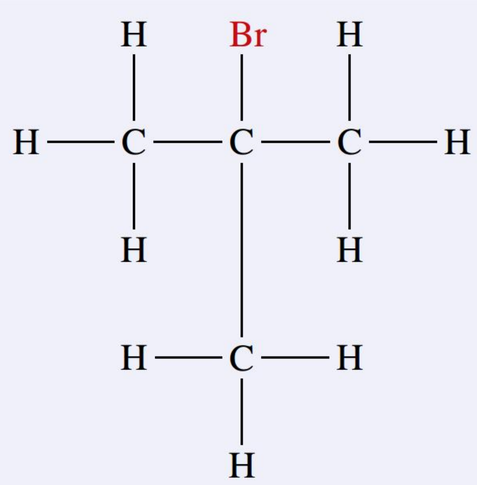
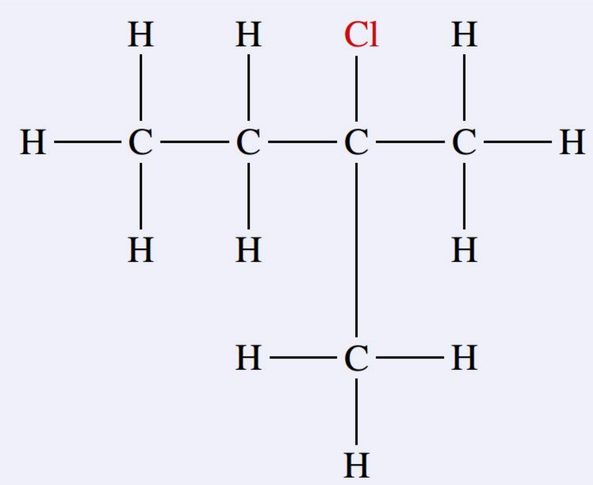
Type of alcohol	Definition	General formula	Examples
primary	The carbon bonded to the halogen is only bonded to one alkyl group.	 where X = F, Cl, Br or I	 
secondary	The carbon bonded to the halogen is also bonded to two alkyl groups.	 where X = F, Cl, Br or I	 
tertiary	The carbon atom bonded to the halogen is also bonded to three alkyl groups.	 where X = F, Cl, Br or I	 

TABLE 8.4.4 Names of the haloalkane functional groups

Halogen	Functional group name
fluorine	fluoro-
chlorine	chloro-
bromine	bromo-
iodine	iodo-

Naming haloalkanes

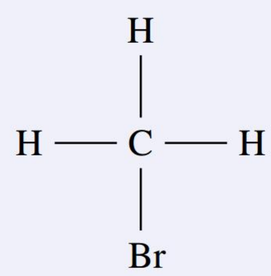
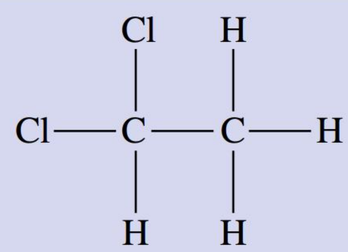
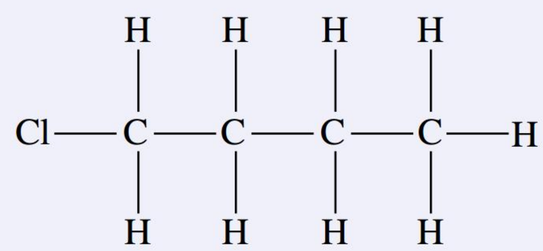
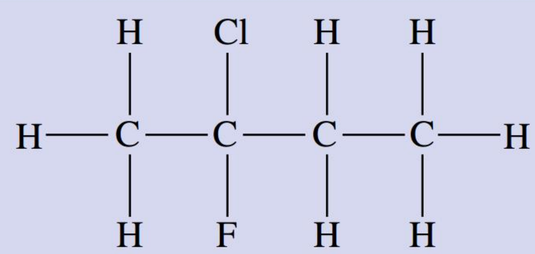
The names of haloalkane functional groups are derived from the name of the halogen, as shown in Table 8.4.4.

The rules for naming haloalkanes follow the rules for naming alkanes. In addition, the following conventions are applied.

- Place the name of the specific halo functional group at the start of the parent alkane's name.
- If positional isomers are possible, number the carbon atoms in the parent chain beginning at the end nearer the first halo group or alkyl side chain (whichever comes first). Use the numbers to indicate the carbon to which the halo functional group is attached. A hyphen should be inserted into the name between a number and a letter.
- In compounds with more than one halo functional group of the same type, number each to show their position in the chain and separate the numbers by a comma. The prefixes 'di-', 'tri-' and 'tetra-' should also be used.
- If more than one type of halo functional group is present, or a halo functional group and an alkyl side chain are present together, list them in alphabetical order.

We can apply these rules to name the haloalkanes listed in Table 8.4.5.

TABLE 8.4.5 Examples of haloalkanes and their names

Name	Condensed structural formula	Extended structural formula
bromomethane	CH_3Br	
1,1-dichloroethane	CH_3CHCl_2	
1-chlorobutane	$CH_3CH_2CH_2CH_2Cl$	
2-chloro-2-fluorobutane	$CH_3CClFCH_2CH_3$	

Alcohols

Ethanol (shown in Figure 8.4.5) is a member of the homologous series of alcohols. Alcohols are found widely in nature and have many uses and applications. For example, ethanol is used as a fuel, a solvent in pharmaceuticals and toiletries, and it is also the alcohol found in alcoholic drinks.

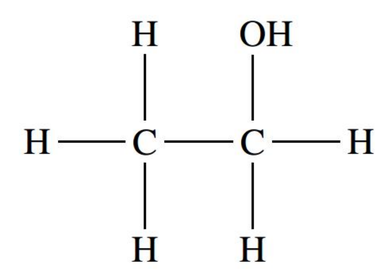


FIGURE 8.4.5 Ethanol is a member of the homologous series of alcohols.

Alcohols contain a hydroxyl (–OH) functional group attached to a saturated carbon atom. A representation of the hydroxyl group is shown in Figure 8.4.6.

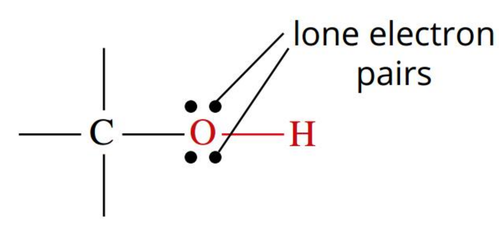
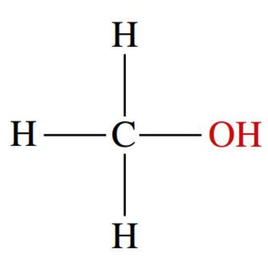


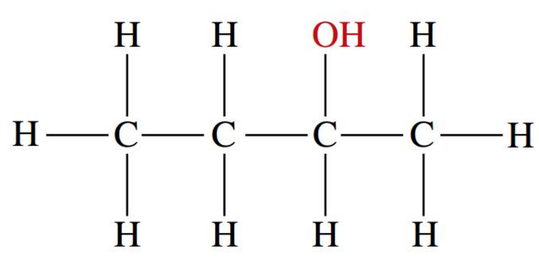
FIGURE 8.4.6 Alcohols contain the hydroxyl functional group –OH (shown in red). There are two pairs of non-bonding electrons on the oxygen atom.

Figure 8.4.7 shows the structural formulas of three more alcohols. You can think of the hydroxyl group as taking the place of a hydrogen atom in an alkane.



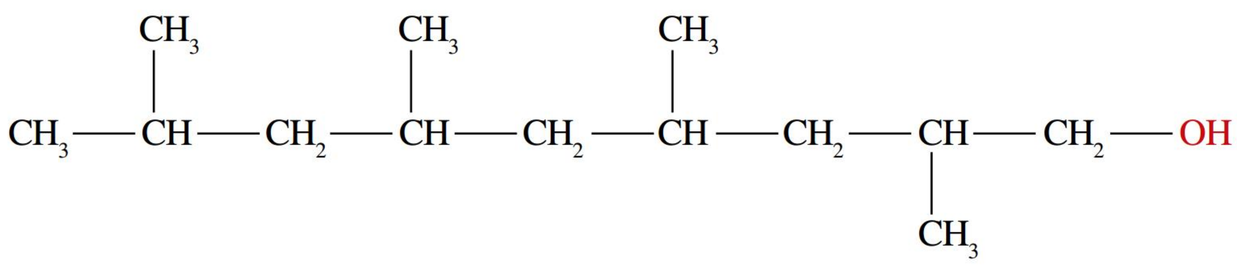
methanol

CH_3OH



butan-2-ol

$CH_3CH_2CHOHCH_3$



2,4,6,8-tetramethylnonan-1-ol

$(CH_3)_2CHCH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_2OH$

FIGURE 8.4.7 Extended and condensed structural formulas of three alcohols. Each contains the hydroxyl functional group (shown in red). Note that the non-bonding electron pairs on the oxygen atom are usually omitted in extended structural formulas.

Alcohols contain a hydroxyl functional group attached to a saturated carbon atom.

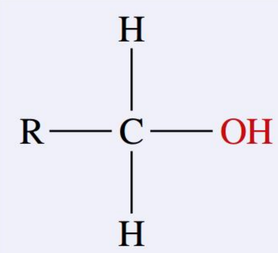
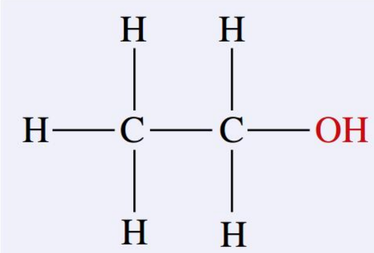
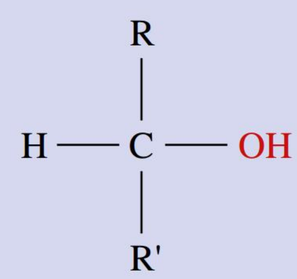
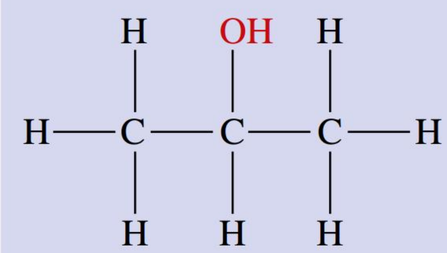
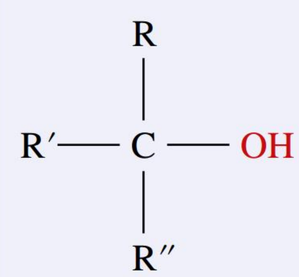
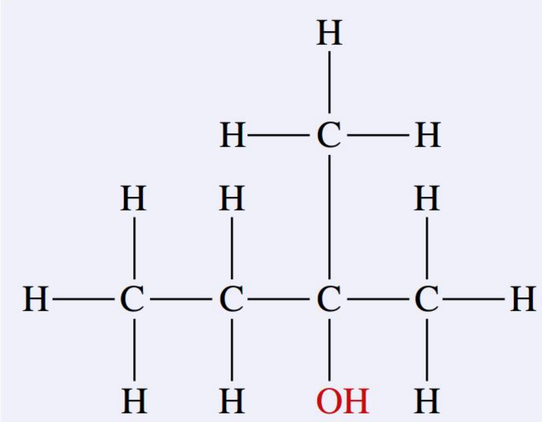
Classifying alcohols

Alcohols are classified according to the number of alkyl chains attached to the carbon bonded to the hydroxyl group (in the same way as haloalkanes). The three different types of alcohols are:

- **primary alcohols**
- **secondary alcohols**
- **tertiary alcohols**.

The definition of each type and examples are shown in Table 8.4.6. Alkyl groups are represented by the general symbols R, R' and R". This classification of alcohols as primary, secondary or tertiary is extremely important because reactions of alcohols, which are discussed in Chapter 9, differ from one class of alcohol to another.

TABLE 8.4.6 The three different types of alcohols. The hydroxyl group is shown in red.

Type of alcohol	Definition	General formula	Example
primary	The carbon atom bonded to the –OH group is only bonded to one alkyl group.		
secondary	The carbon atom bonded to the –OH group is also bonded to two alkyl groups.		
tertiary	The carbon atom bonded to the –OH group is also bonded to three alkyl groups.		

Naming alcohols

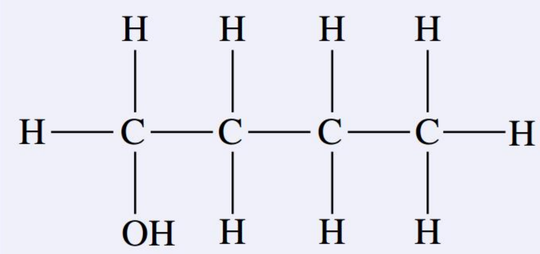
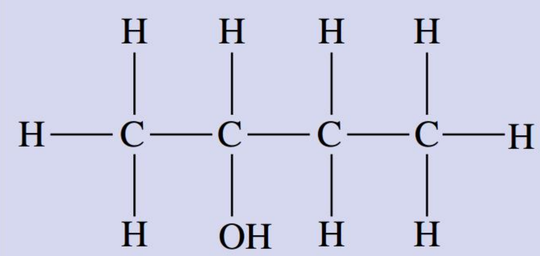
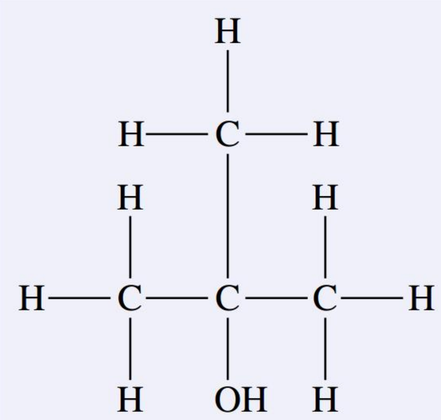
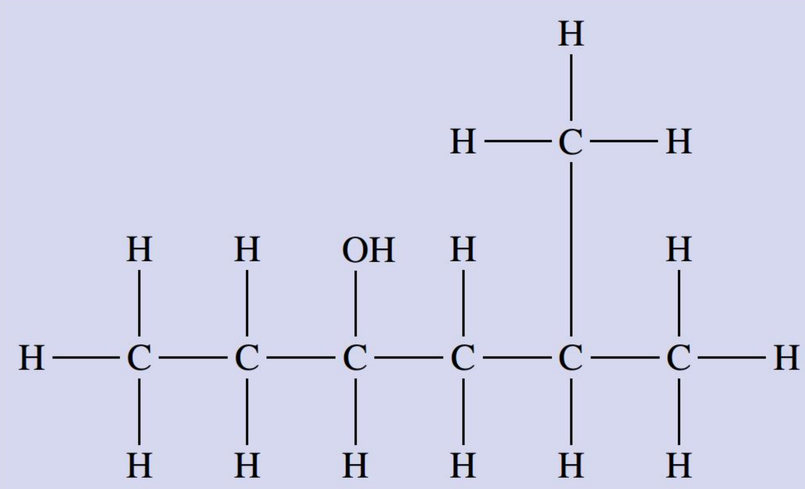
Alcohol names follow the rules used for alkanes, except that the '-e' at the end of the parent alkane's name is replaced with the suffix '-ol'.

The following rules also apply.

- Identify the parent name from the longest carbon chain containing the hydroxyl group.
- If positional isomers are possible, a number is inserted before the '-ol' to indicate the carbon to which the hydroxyl functional group is attached.
- Number the carbon chain commencing at the end closest to the hydroxyl group. In numbering the carbon chain, the hydroxyl group takes priority over any alkyl side chains, so if there is more than one numbering option, the name in which the hydroxyl group is the smallest is correct.

We can apply these rules to name the alcohols listed in Table 8.4.7. Notice that the first three alcohols in the table are all structural isomers of $C_4H_{10}O$. The last alcohol illustrates the priority that the hydroxyl group takes over alkyl side chains when numbering the carbon chain.

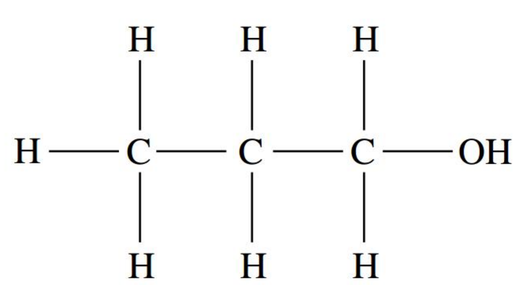
TABLE 8.4.7 Examples of naming alcohols

Name	Molecular formula	Condensed structural formula	Extended structural formula
butan-1-ol	$C_4H_{10}O$	$CH_3CH_2CH_2CH_2OH$	 This is an example of a primary alcohol.
butan-2-ol	$C_4H_{10}O$	$CH_3CHOHCH_2CH_3$	 This is an example of a secondary alcohol.
2-methylpropan-2-ol	$C_4H_{10}O$	$(CH_3)_3COH$	 This is an example of a tertiary alcohol.
5-methylhexan-3-ol	$C_7H_{16}O$	$CH_3CH_2CHOHCH_2CH(CH_3)CH_3$	 This is an example of a secondary alcohol.

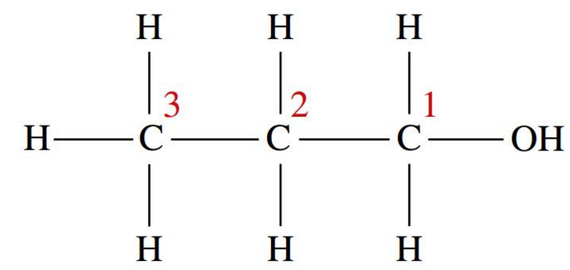
Worked example 8.4.1

IUPAC NAMING SYSTEM FOR ALCOHOLS

Use systematic naming rules to determine the name of the following alcohol.



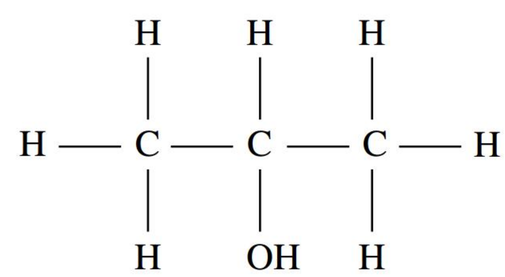
Thinking	Working
Identify the longest carbon chain in the molecule. The name of the molecule is based on this longest chain.	There are three carbon atoms in the longest chain. The name is based on propane.

Identify the functional group present and the suffix to use at the end of the molecule's name.	There is a hydroxyl group present. The molecule is an alcohol so the suffix is '-ol'.
Number the carbon atoms starting from the end closest to the hydroxyl functional group.	
Identify the position(s) and type(s) of alkyl side chains.	There are no alkyl side chains in this molecule.
Combine all components. Place the number for the position of the hydroxyl group in front of the '-ol' ending.	The name of the molecule is propan-1-ol.

➤ Try yourself 8.4.1

IUPAC NAMING SYSTEM FOR ALCOHOLS

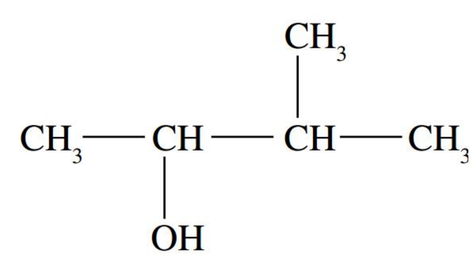
Use systematic naming rules to determine the name of the following alcohol.



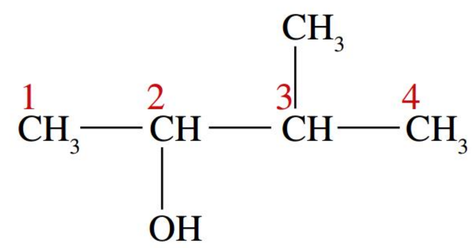
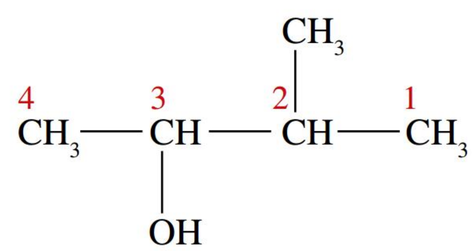
Worked example 8.4.2

NAMING ALCOHOLS THAT CONTAIN ALKYL SIDE CHAINS

Determine the systematic name for the following molecule.



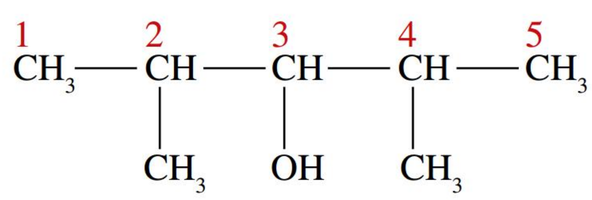
Thinking	Working
Identify the longest carbon chain in the molecule. The name of the molecule is based on this longest chain.	There are four carbon atoms in the longest chain. The name is based on butane.
Identify the functional group present and the suffix to use at the end of the molecule's name.	There is a hydroxyl group present. The molecule is an alcohol, so the suffix is '-ol'.

Number the carbon atoms starting from the end closest to the functional group. Remember that the hydroxyl group takes priority over the alkyl side chains, so make sure you do not number the carbon atoms starting from the wrong end.	 correct numbering  incorrect numbering
Identify the position(s) and the type(s) of alkyl side chains.	There is a methyl ($-CH_3$) group on carbon number 3, so the prefix 'methyl-' will be used.
Combine all components. Place the number for the position of the alkyl side chain in front of the prefix, and the number for the position of the hydroxyl group in front of the '-ol' ending.	The name of the molecule is 3-methylbutan-2-ol.

➤ Try yourself 8.4.2

NAMING ALCOHOLS THAT CONTAIN ALKYL SIDE CHAINS

Determine the systematic name for the following molecule.



Amines

Amines are a class of organic compounds that contain the **amino functional group**. In **primary amines**, the amino functional group consists of one nitrogen atom covalently bonded to two hydrogen atoms, as shown in Figure 8.4.8.

Amino functional groups with two hydrogens and one alkyl group are called primary amines. Amines are classified as 'primary', 'secondary' and 'tertiary' according to the number of alkyl groups attached to the nitrogen atom (Note the difference in convention between classifying alcohols and haloalkanes vs amines.). Secondary and tertiary amines exist, but these compounds are not covered in this course. Some primary amines are shown in Figure 8.4.9.

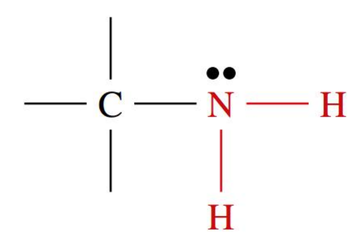


FIGURE 8.4.8 Primary amines contain the amino functional group $-NH_2$ (shown in red). There are two non-bonding electrons on the nitrogen atom.

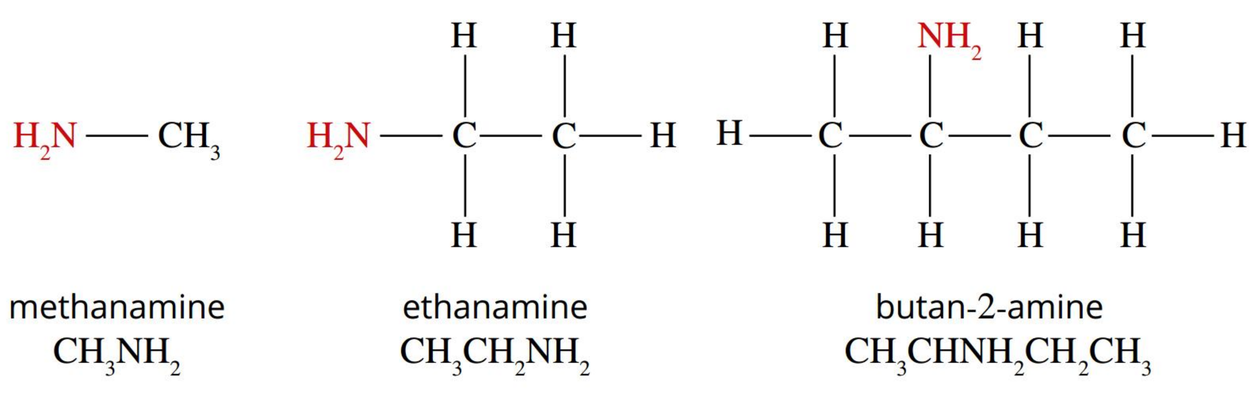


FIGURE 8.4.9 Extended and condensed structural formulas of three primary amines. The amino functional group is shown in red. Primary amines have one carbon atom bonded to the nitrogen atom. Note that the naming of amines is not required for this course.

Primary amines consist of an amino functional group in which one nitrogen atom is covalently bonded to two hydrogen atoms.

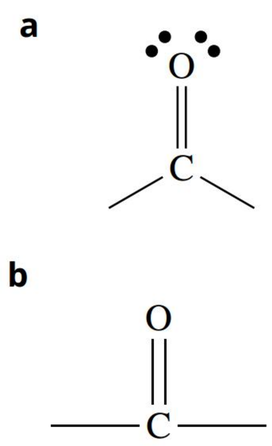


FIGURE 8.4.10 The carbonyl functional group. The non-bonding pairs of electrons shown on the oxygen atom are often not included in structural formulas.

HYDROCARBON DERIVATIVES WITH THE CARBONYL GROUP

We will now focus on five classes of compounds which contain the carbonyl functional group. As discussed earlier in the module, a carbonyl functional group, shown in Figure 8.4.10a, consists of a carbon atom connected to an oxygen atom by a double bond. All atoms bonded to the carbon atom are in a plane and the angles between the bonds are 120°. However, for convenience, the bonds are often drawn at right angles and the non-bonding pairs of electrons are not included, as shown in Figure 8.4.10b.

As shown in Figure 8.4.11, the compounds containing this carbonyl group are aldehydes, ketones, carboxylic acids, esters and amides. These compounds are prevalent in nature and they also have a wide variety of uses in industrial, pharmaceutical and cosmetic applications.

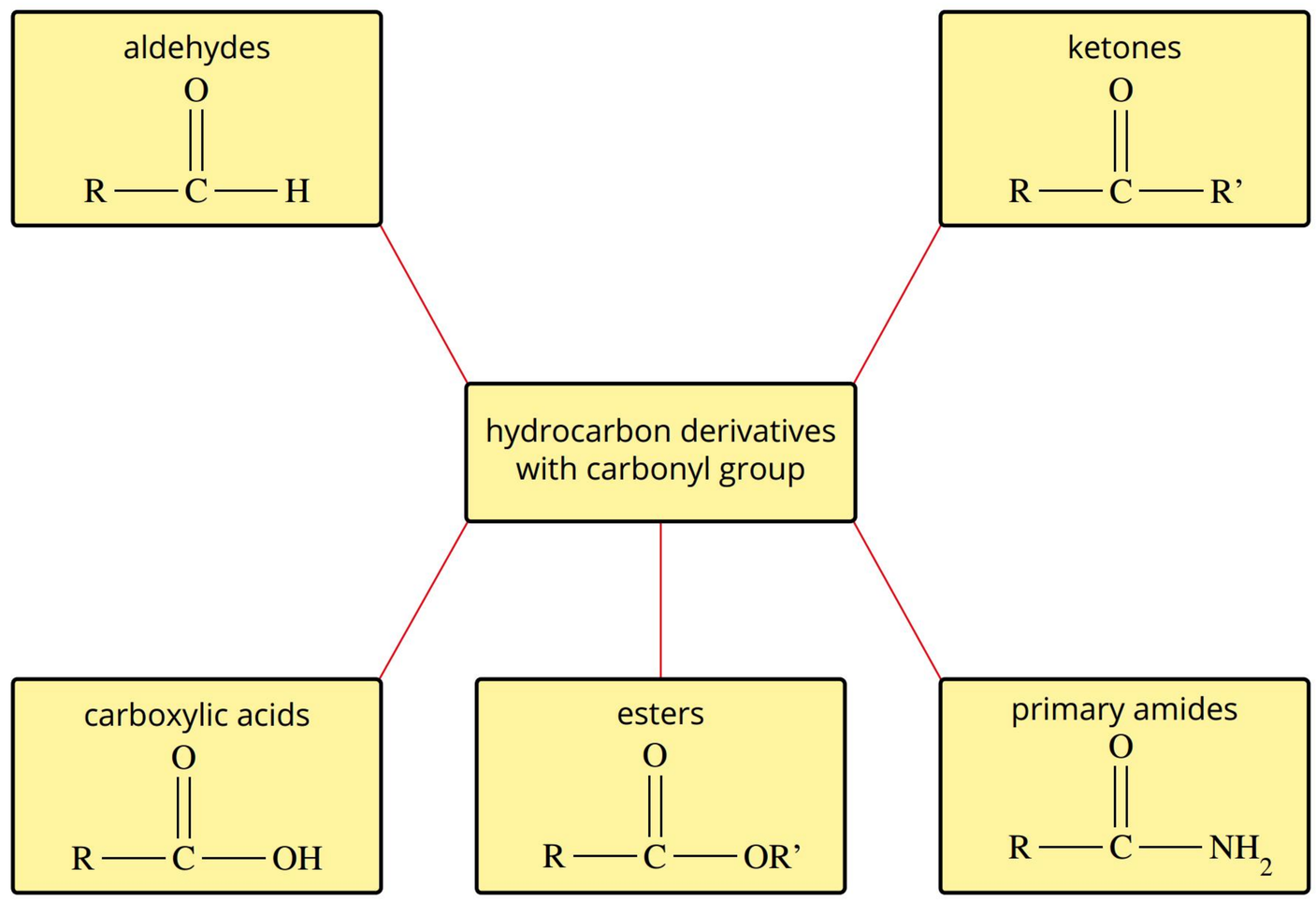


FIGURE 8.4.11 Five classes of hydrocarbon derivatives that contain the carbonyl group

Aldehydes contain a carbonyl functional group attached to a hydrogen atom at the end of the carbon chain.

Aldehydes

In aldehydes, the carbonyl group is always at the end of the hydrocarbon chain because the carbon atom of the carbonyl group is bonded to a hydrogen atom. The carbonyl functional group in an aldehyde is written as –CHO at the end of the condensed structural formula of aldehydes.

The simplest aldehyde, HCHO, is methanal (commonly known as formaldehyde) and is used to preserve biological specimens, including embalming human remains. The structural formulas of methanal and two other aldehydes are shown in Figure 8.4.12.

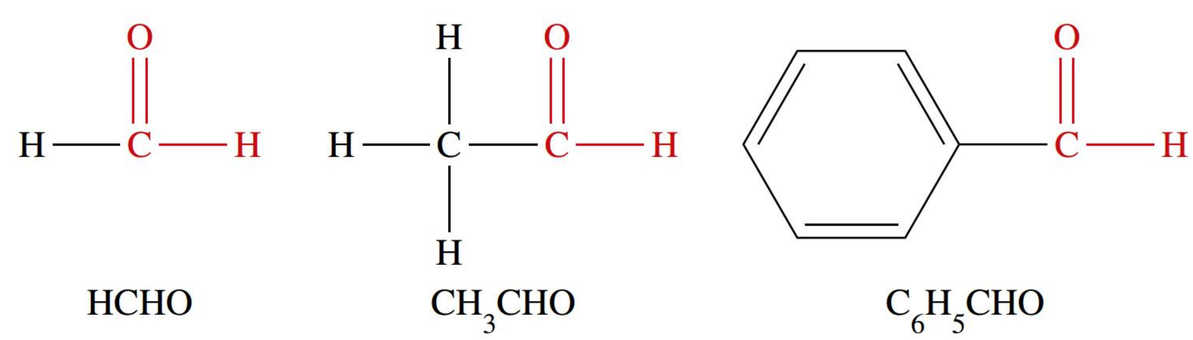


FIGURE 8.4.12 Extended and condensed structural formulas of three aldehydes. Each contains a carbonyl functional group with a hydrogen atom attached, shown in red.

Naming aldehydes

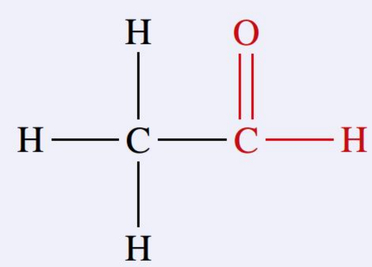
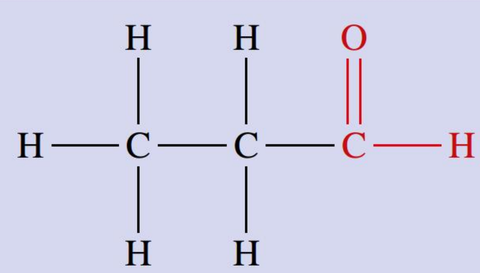
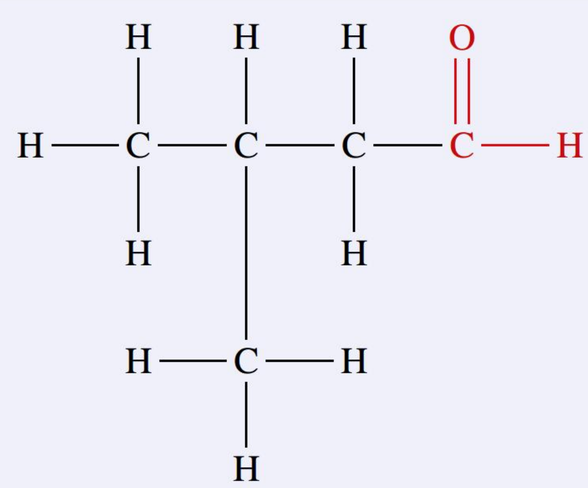
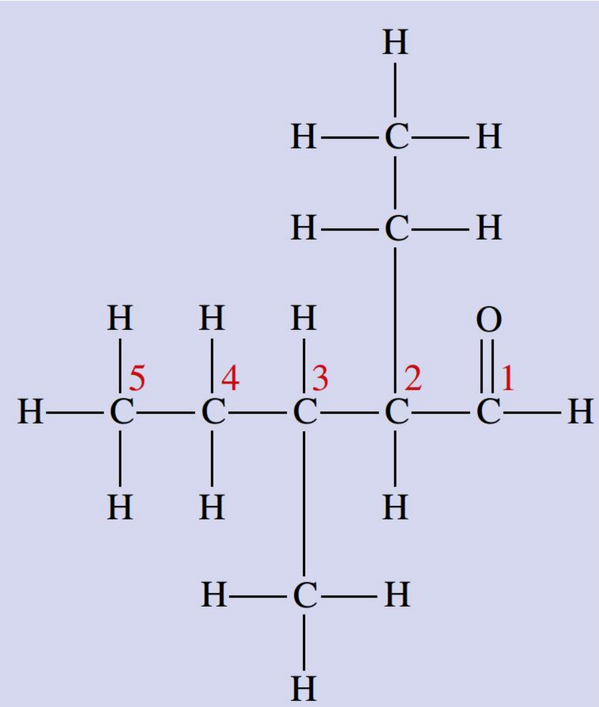
Aldehyde names follow the rules used for alkanes, except that the '-e' at the end of the parent alkane's name is replaced with the suffix '-al'.

The following rules also apply.

- Identify the parent name from the longest carbon chain containing the carbonyl group.
- Number the carbon chain so that the carbonyl carbon atom is the first carbon in the chain (carbon number 1).
- The position of the carbonyl functional group does not need to be specified as it will always be on the first carbon.

Table 8.4.8 lists the names of four different aldehydes.

TABLE 8.4.8 Examples of naming aldehydes

Name	Molecular formula	Condensed structural formula	Extended structural formula
ethanal	C_2H_4O	CH_3CHO	
propanal	C_3H_6O	CH_3CH_2CHO	
3-methylbutanal	$C_5H_{10}O$	$CH_3CH(CH_3)CH_2CHO$	
2-ethyl-3-methylpentanal	$C_8H_{16}O$	$CH_3CH_2CH(CH_3)CH(CH_2CH_3)CHO$	 Note that the longest chain that contains the functional group is five carbons long.

Ketones

In ketones, the carbonyl carbon is attached to two other carbon atoms. This means that the carbonyl group is never at the end of the molecule. In condensed structural formulas, the carbonyl functional group in a ketone is simply written as –CO–.

The simplest ketone, CH_3COCH_3, is commonly called acetone (its IUPAC systematic name is propan-2-one) and is a useful polar organic solvent, frequently found in nail polish remover and paint thinner. Figure 8.4.13 shows the extended structural formulas of three ketones. The carbonyl group in each is highlighted in red.

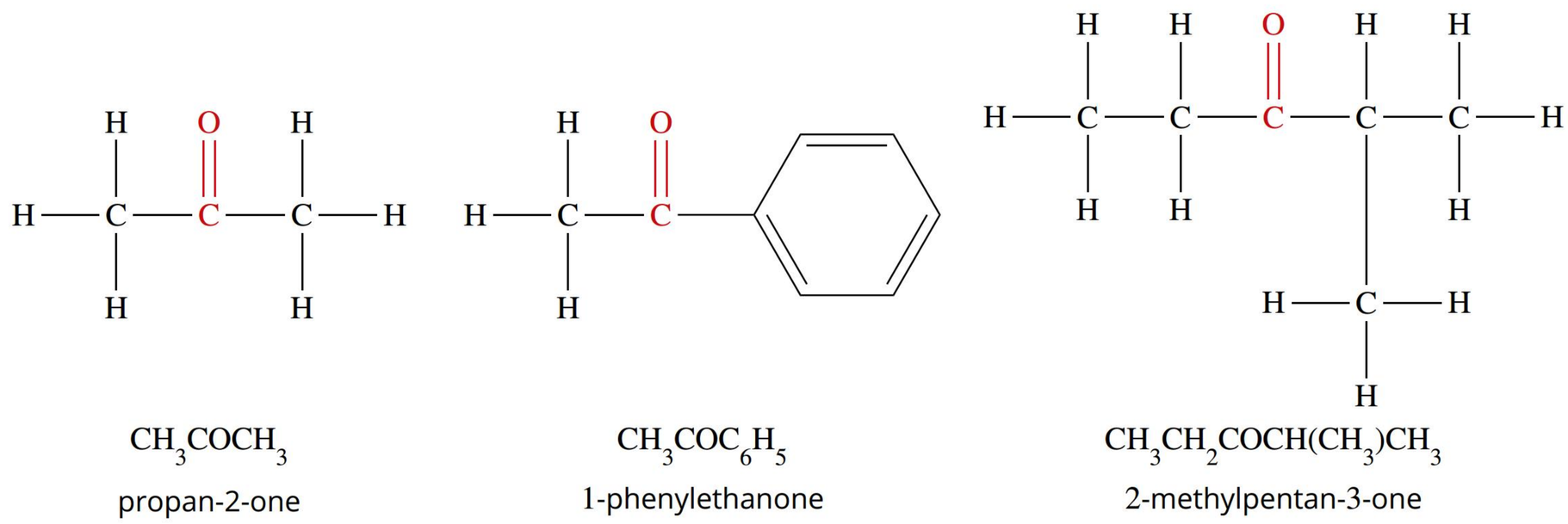


FIGURE 8.4.13 Extended and condensed structural formulas of three ketones. Each contains a carbonyl functional group (shown in red) attached to two hydrocarbon groups.

Ketones contain a carbonyl group attached to two other carbon atoms; the carbonyl group is never at the end of the carbon chain.

Naming ketones

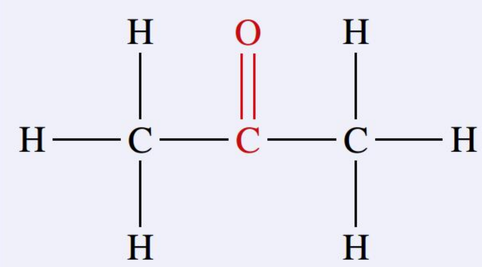
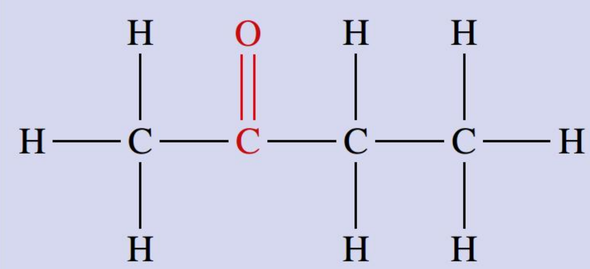
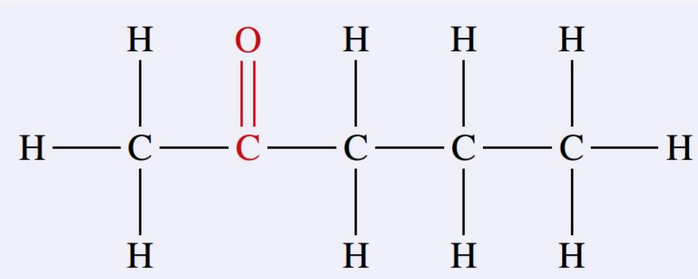
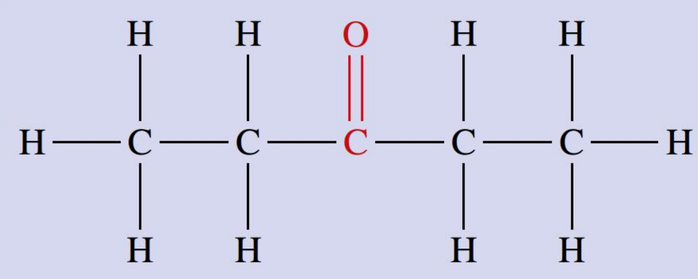
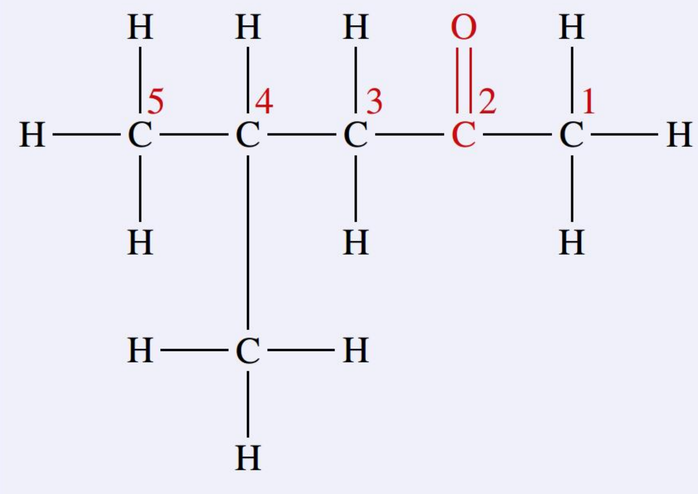
Ketone names follow the rules used for alkanes, except that the '-e' at the end of the parent alkane's name is replaced with the suffix '-one'.

The following rules also apply.

- Identify the parent name from the longest carbon chain containing the carbonyl group.
- Number the carbon chain commencing at the end closest to the carbonyl group.
- If positional isomers are possible, use numbers to indicate the position of the carbonyl group in the molecule. This will be the case for ketones that contain five or more carbon atoms in the parent chain.

Table 8.4.9 lists the names of five different ketones. Pentanone, which is a ketone made up of five carbon atoms, has two positional isomers. These isomers are named pentan-2-one and pentan-3-one; the number in each name represents the position of the carbonyl group in the molecule. It is also important to note that in 4-methylpentan-2-one, the carbonyl carbon takes priority over the methyl side chain when numbering the main carbon chain and is therefore assigned the lowest number. If the carbon chain was numbered the opposite way, then the carbonyl carbon would be on carbon number 4 and the ketone would be named 2-methylpentan-4-one, which is incorrect.

TABLE 8.4.9 Examples of naming ketones

Name	Molecular formula	Condensed structural formula	Extended structural formula
propan-2-one	C_3H_6O	CH_3COCH_3	
butan-2-one	C_4H_8O	$CH_3COCH_2CH_3$	
pentan-2-one	$C_5H_{10}O$	$CH_3COCH_2CH_2CH_3$	
pentan-3-one	$C_5H_{10}O$	$CH_3CH_2COCH_2CH_3$	
4-methylpentan-2-one	$C_6H_{12}O$	$CH_3CH(CH_3)CH_2COCH_3$	

Carboxylic acids

Carboxylic acids are a homologous series that contain the carboxyl functional group. The carboxyl functional group (Figure 8.4.14) consists of a carbonyl group attached to a hydroxyl group.

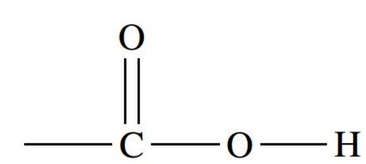


FIGURE 8.4.14 Structure of the carboxyl functional group

The **carboxyl functional group** is represented in a condensed structural formula as –COOH and is always located at one end of a hydrocarbon chain. Carboxylic acids are prevalent in nature and are also very useful in the food and pharmaceutical industries. Figure 8.4.15 shows the extended structural and condensed structural formulas of three carboxylic acids. Methanoic acid is the simplest carboxylic acid (commonly called formic acid) and is found in some ant stings. Ethanoic acid (commonly called acetic acid) is the chief component of vinegar, and lactic acid is found in sour milk and is also formed in muscles during exercise. Longer chain carboxylic acids (known as fatty acids) are used in the production of soaps and other cleansing products.

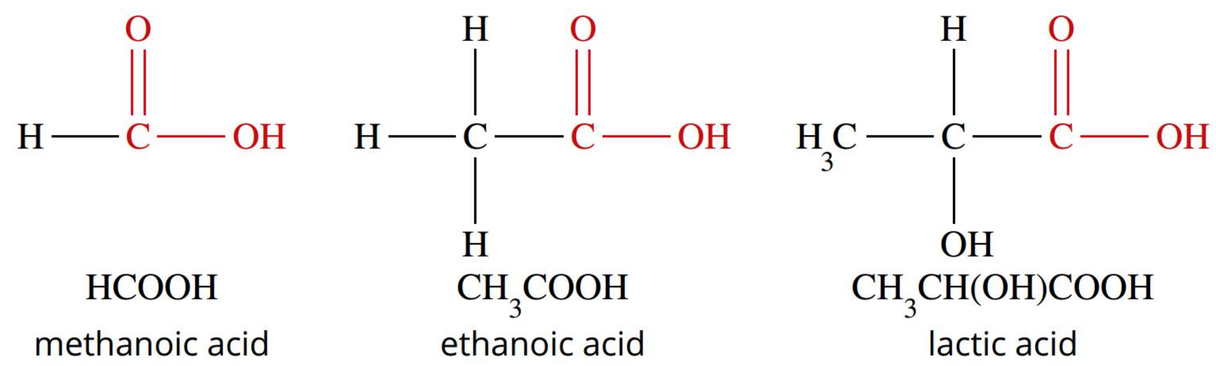


FIGURE 8.4.15 Extended structural and condensed structural formulas of three carboxylic acids. Each contains a carboxyl functional group shown in red.

Naming carboxylic acids

Carboxylic acids follow the rules used for alkanes, except that the '-e' at the end of the parent alkane's name is replaced with the suffix '-oic acid'.

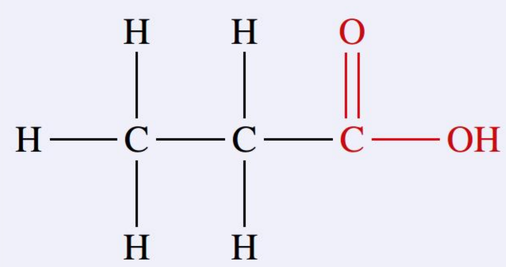
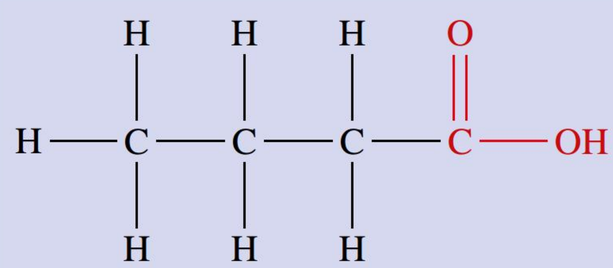
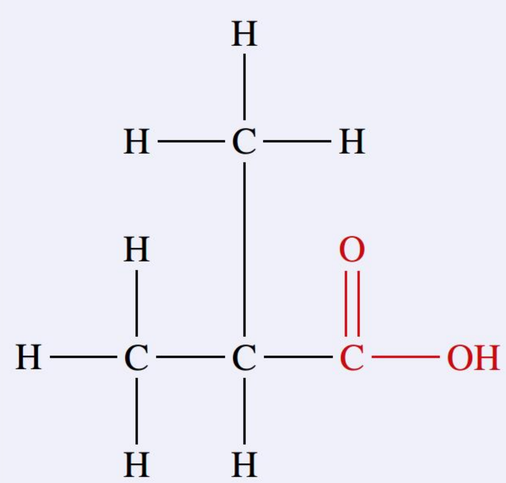
The following rules also apply.

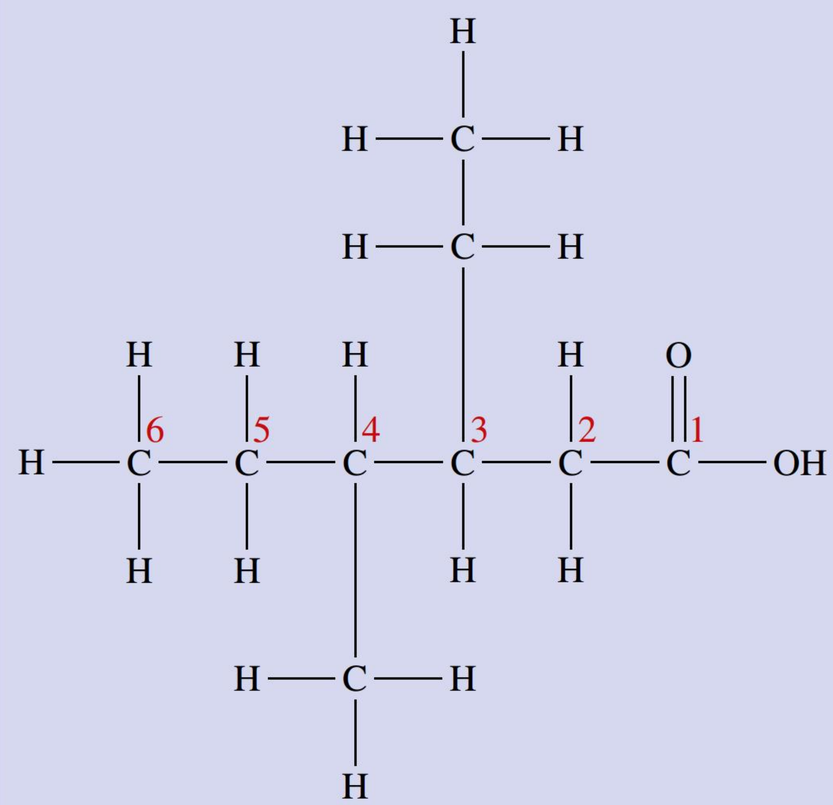
- Identify the parent name from the longest carbon chain containing the carboxyl group.
- Number the carbon chain so that the carboxyl carbon atom is the first carbon in the chain (carbon number 1).
- The position of the carboxyl functional group does not need to be specified as it will always be on the first carbon.

Table 8.4.10 lists the names of four different carboxylic acids. Notice that butanoic acid and 2-methylpropanoic acid are isomers with the molecular formula $C_4H_8O_2$.

Carboxylic acids contain a carboxyl functional group made up of a carbonyl group attached to a hydroxyl group. The carboxyl functional group is always located at the end of the carbon chain.

TABLE 8.4.10 Examples of naming carboxylic acids

Name	Molecular formula	Condensed structural formula	Extended structural formula
propanoic acid	$C_3H_6O_2$	CH_3CH_2COOH	
butanoic acid	$C_4H_8O_2$	$CH_3CH_2CH_2COOH$	
2-methylpropanoic acid	$C_4H_8O_2$	$CH_3CH(CH_3)COOH$	

Name	Molecular formula	Condensed structural formula	Extended structural formula
3-ethyl-4-methylhexanoic acid	$C_9H_{18}O_2$	$CH_3CH_2CH(CH_3)CH(CH_2CH_3)CH_2COOH$	

Esters

Esters are a class of organic compounds that contain a carbonyl (C=O) group attached to an oxygen that is linked to another carbon. The **ester functional group** (shown in Figure 8.4.16) is similar to a carboxyl functional group, but the hydrogen of the –OH is replaced by an alkyl group. In condensed structural formulas, the ester is usually written as –COO–.

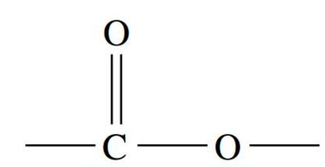


FIGURE 8.4.16 Structure of the ester functional group

Esters are compounds that often have characteristic sweet, fruity odours. Many esters occur naturally in fruits and flowers. The distinctive and appealing odour of your favourite perfume or aftershave may well be due to esters.

Figure 8.4.17 shows the extended structural and condensed structural formulas of three esters. Propyl ethanoate smells like pears, whereas pentyl ethanoate is responsible for the odour of bananas. Acetylsalicylic acid is a very important ester; its common name is aspirin and is used in large quantities as a painkiller.

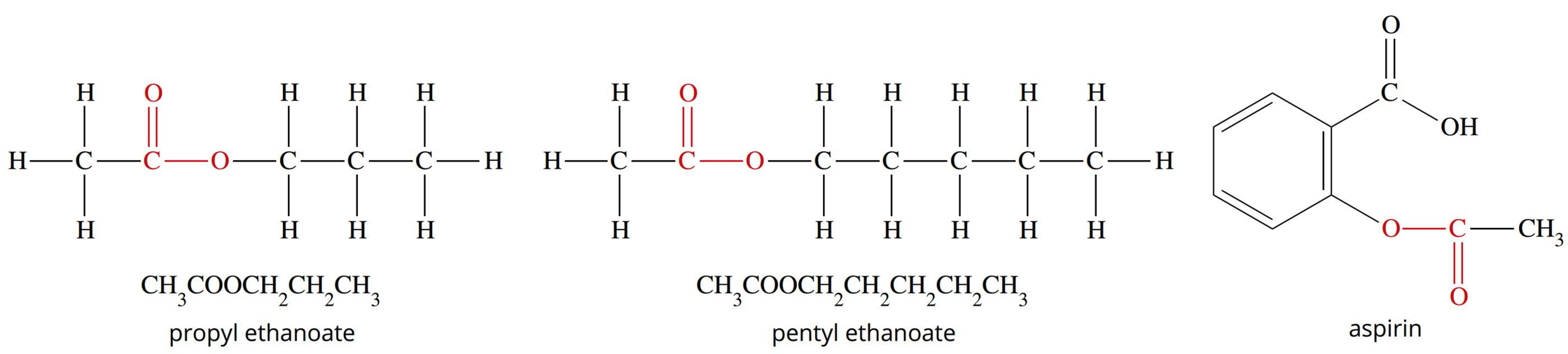


FIGURE 8.4.17 The structures of three different esters. The ester functional group is shown in red. It contains a carbonyl functional group attached to an oxygen atom.

Naming esters

The systematic IUPAC naming of esters follows different conventions than the naming of compounds in the other homologous series that have been discussed so far. Esters are produced by the reaction of a carboxylic acid with an alcohol (this reaction will be discussed in more detail in Chapter 9). There are two parts to an ester's name and it is built up from the names of the carboxylic acid and alcohol that reacted to form it. The first word, derived from the alcohol, is based on the number of carbon atoms in the chain attached to the singly bonded (–O–). The second word of the name, derived from the carboxylic acid, is based on the number of carbon atoms in the chain containing the carbonyl group.

The ester functional group is similar to the carboxyl functional group except that the hydrogen of the –OH is replaced with an alkyl group.

In the example shown in Figure 8.4.18, an ester is produced from the carboxylic acid propanoic acid and the alcohol methanol.

We can determine the name of this ester using the following steps:

- The alkyl group bonded to the –O– is named first. This is the word derived from the alcohol.
- The carbonyl section of the ester makes up the second word of the name and is derived from the carboxylic acid. The name of the carboxylic acid is adapted by changing the '-oic acid' suffix to '-oate'.

Using these rules, you can work out that the name of the ester shown in Figure 8.4.18 is methyl propanoate.

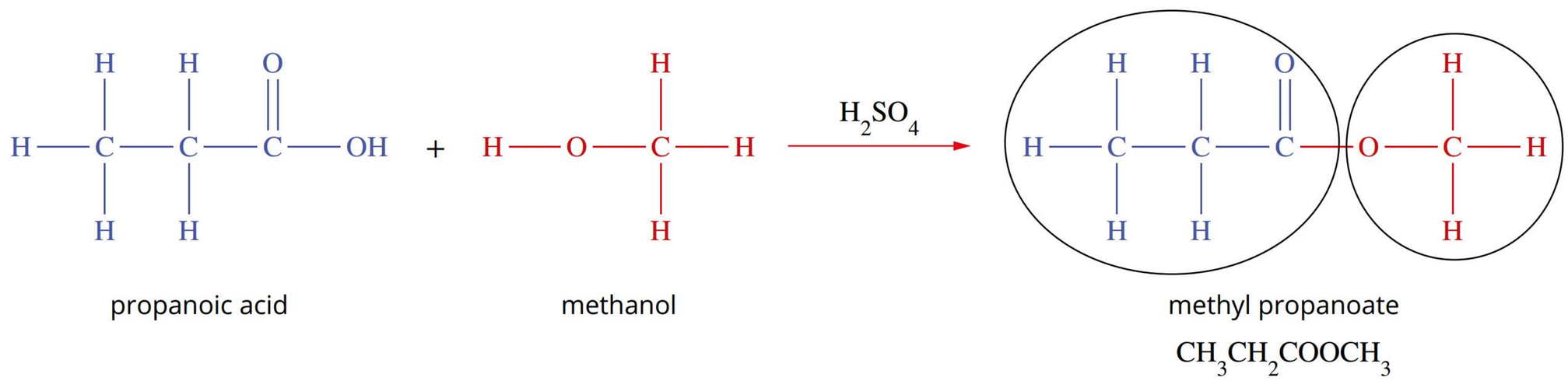
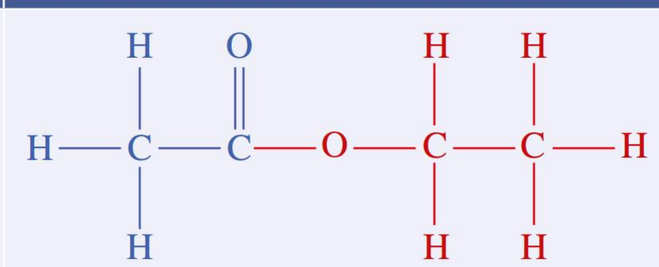
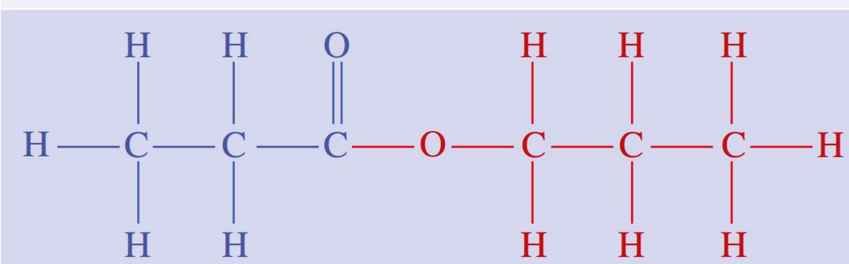
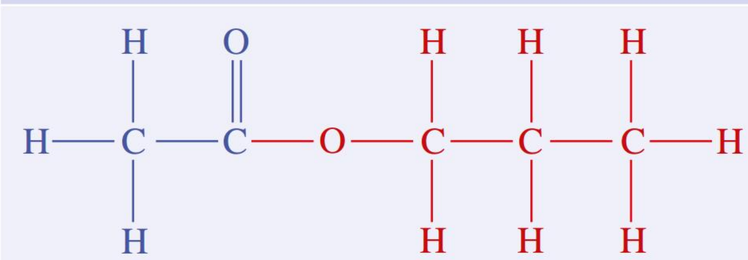


FIGURE 8.4.18 The name of an ester is derived from the names of the alcohol and carboxylic acid from which it is built.

The names and formulas of three more esters are shown in Table 8.4.11, with the part of each molecule derived from the alcohol in red and the part derived from the carboxylic acid in blue.

TABLE 8.4.11 Examples of naming esters

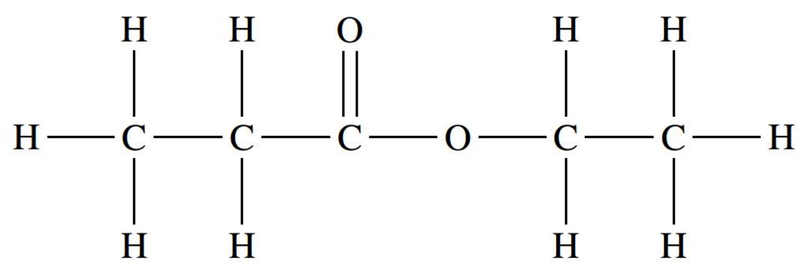
Name	Molecular formula	Condensed structural formula	Extended structural formula
ethyl ethanoate	$C_4H_8O_2$	$CH_3COOCH_2CH_3$	
propyl propanoate	$C_6H_{12}O_2$	$CH_3CH_2COOCH_2CH_2CH_3$	
propyl ethanoate	$C_5H_{10}O_2$	$CH_3COOCH_2CH_2CH_3$	

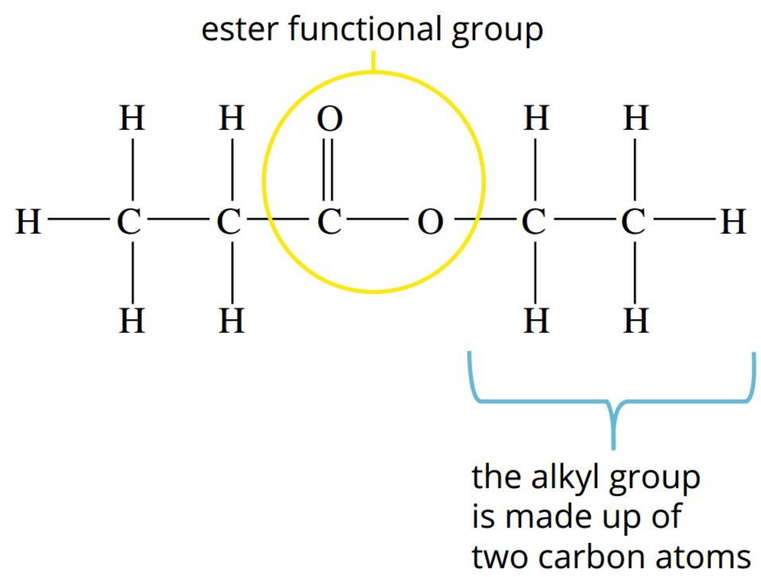
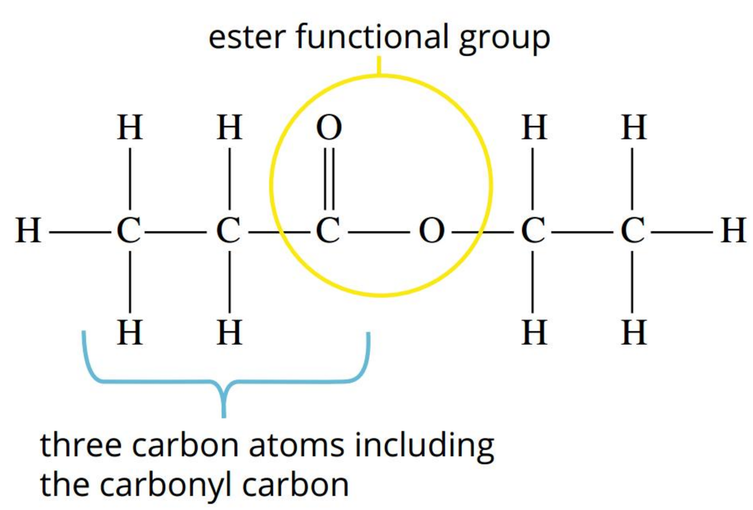
Use Worked example 8.4.3 to develop your skills in naming esters.

Worked example 8.4.3

IUPAC NAMING SYSTEM FOR ESTERS

Determine the systematic name for the following molecule.

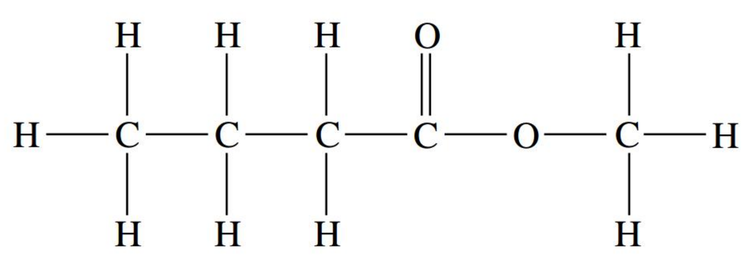


Thinking	Working
Locate the ester functional group. Identify the name of the alkyl group bonded to the –O– section of the ester functional group (this is the name derived from the alcohol). In this case, the alkyl group is made up of two carbon atoms.	 The alkyl group is named 'ethyl'. This is the first word of the ester name.
Starting from the carbonyl carbon, identify the number of carbon atoms in the chain attached to it. From the name of the corresponding carboxylic acid, replace the '-oic acid' with '-oate'.	 There are three carbon atoms in the chain, including the carbonyl carbon. The carboxylic acid with three carbon atoms is propanoic acid. From this name, change the '-oic acid' suffix to '-oate'. This gives 'propanoate', which is the second word of the ester name.
Combine the two components, placing the alkyl part of the name first.	The name of the molecule is ethyl propanoate.

➤ Try yourself 8.4.3

IUPAC NAMING SYSTEM FOR ESTERS

Determine the systematic name for the following molecule.



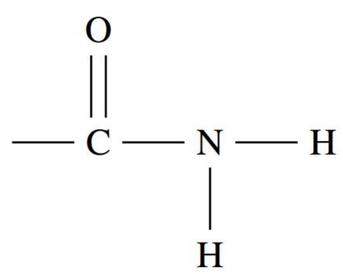


FIGURE 8.4.19 Structure of the amide functional group in a primary amide

Amides

Primary amides contain a carbonyl functional group attached to an amino functional group. They are similar to carboxyl groups, except that the –OH is replaced with $–NH_2$, as shown in Figure 8.4.19.

The nitrogen atom in primary amides is bonded to two hydrogen atoms. Secondary and tertiary amides exist; Chapter 9 describes the synthesis of a secondary amide from the reaction of a carboxylic acid with an amine. The **amide functional group** is represented in a condensed structural formula as $–CONH_2$ and is always located at one end of a hydrocarbon chain. The extended structural and condensed structural formulas of three primary amides are shown in Figure 8.4.20.

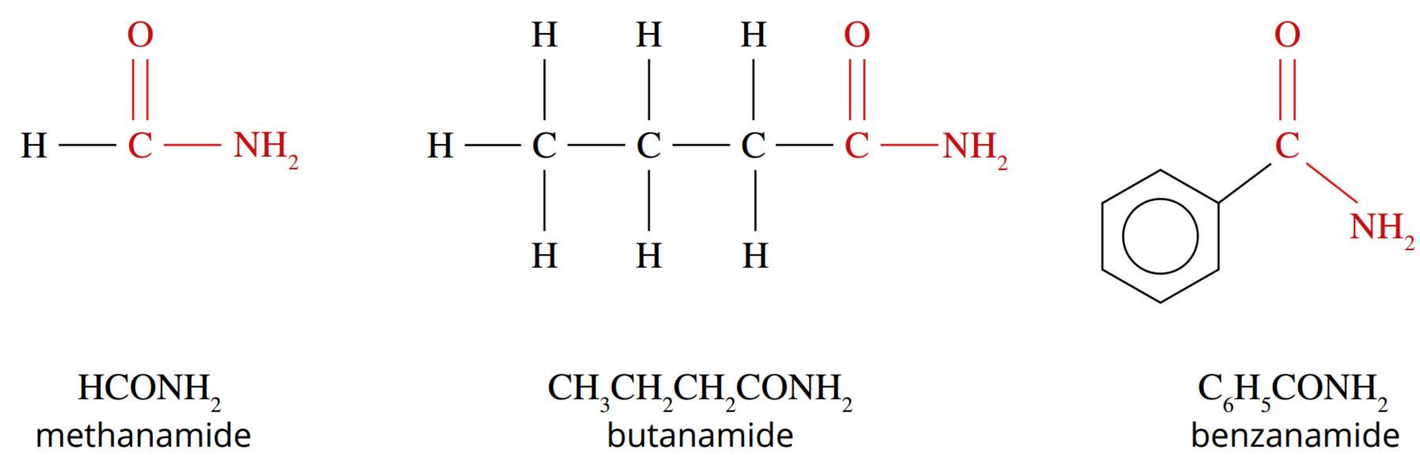


FIGURE 8.4.20 Extended structural and condensed structural formulas of three amides, with the amide functional group shown in red. (Note that the naming of amides is not required for this course.)

Amides are found widely in nature and are also used extensively in various industries, such as the pharmaceutical industry, the plastic industry and the paper industry. Proteins are polyamides and are described in Chapter 10; they are macromolecules containing many amide functional groups.

Amides contain a carbonyl functional group attached to an amine functional group. Primary amides have the condensed structural formula $–CONH_2$.

8.4 Review

SUMMARY

- Hydrocarbon derivatives have a hydrocarbon skeleton but contain functional groups in which one or more hydrogen atoms have been replaced with other atoms or groups of atoms that give an organic compound its characteristic properties.
- There are millions of known organic compounds but they can be organised into a relatively small number of classes (or homologous series) based on the functional groups present in their molecules.
- Haloalkanes are a homologous series derived from alkanes, in which one hydrogen atom is replaced with a halogen atom.
- Haloalkanes can be classified as primary, secondary or tertiary depending on the number of alkyl groups attached to the carbon atom bonded to the halogen atom.
- Alcohols contain a hydroxyl (–OH) functional group attached to a saturated carbon atom.
- Alcohols can be classified as primary, secondary or tertiary depending on the number of alkyl groups attached to the carbon atom bonded to the hydroxyl group.
- Primary amines contain an amino functional group that consists of a nitrogen atom covalently bonded to two hydrogen atoms.
- Haloalkanes and alcohols can be regarded as being derived from alkanes. The name of the parent alkane is used as the basis for their names. (Note that the naming of amines is not required for this course.)
  - Haloalkanes are named by adding the prefix for the halogen.
  - Alcohols are named by replacing the 'e' at the end of the parent alkane with the suffix '-ol'.
  - When positional isomers exist, a number is used to specify the position of the functional group.
- The carbonyl group (–C=O) is a component of a number of functional groups.
- Aldehydes and ketones are a homologous series that contain a carbonyl group on its own.

- The carbonyl group is at the end of a hydrocarbon chain in aldehydes and within a hydrocarbon chain in ketones.
- Aldehydes are named using the suffix '-al' and ketones are named using the suffix '-one'.
- Carboxylic acids are a homologous series of molecules that contain the carboxyl group (–COOH) at the end of a hydrocarbon chain.
- Carboxylic acids are named using the suffix '-oic acid'.
- Esters are a homologous series of molecules that contain an ester group (–COO–) within the hydrocarbon chain.
- Esters have a two-word name:
  - The alkyl group bonded to the –O– is named first. This name is derived from the alcohol that formed the new compound, with the '-ol' suffix changing to '-yl'.
  - The carbonyl section of the ester makes up the second word of the name and is derived from the carboxylic acid. The name of the carboxylic acid is adapted by changing the '-oic acid' suffix to '-oate'.
- Primary amides are a homologous series of molecules that contain the amide group ($–CONH_2$) at the end of the hydrocarbon chain.

KEY QUESTIONS

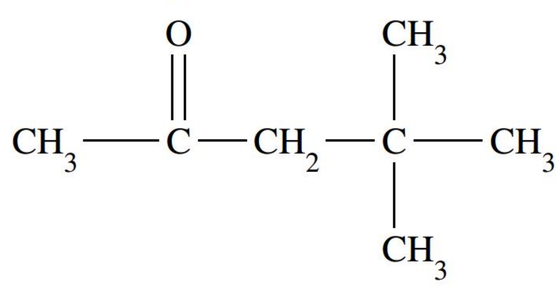
Describe

1 **a** Define a carbonyl group.

b Name the classes of organic compounds in which the carbonyl group is found.

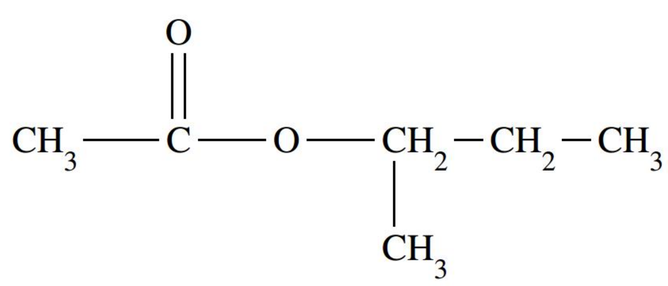
2 Identify the class of organic compound that each of the following molecules belongs to.

a



b $CH_3–CH_2–CH_2–OH$

c



Apply

3 Describe each of the following classes of organic compounds by stating the parent class they are derived from and the functional group that is present in each.

a haloalkane

b alcohol

4 Provide a structural formula of the functional group in each of the following classes of compounds.

a aldehyde

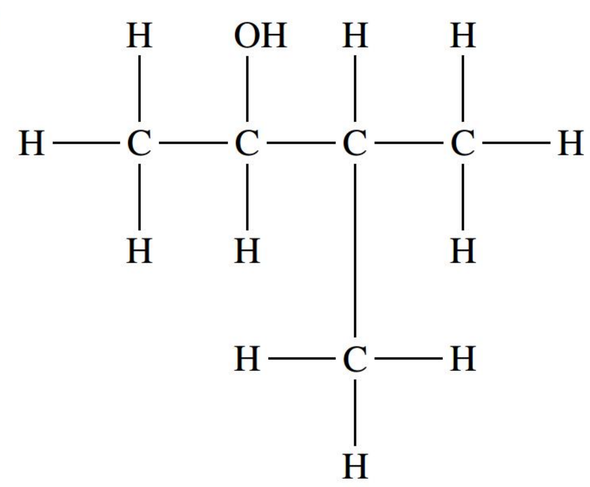
b carboxylic acid

c ester

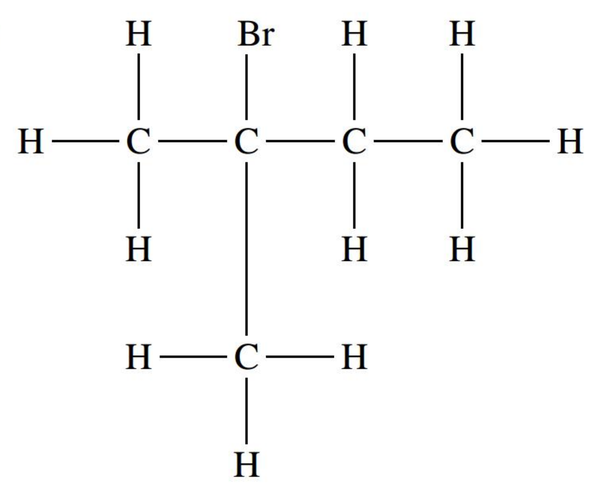
Analyse

5 Classify the following alcohols and haloalkanes as primary, secondary or tertiary.

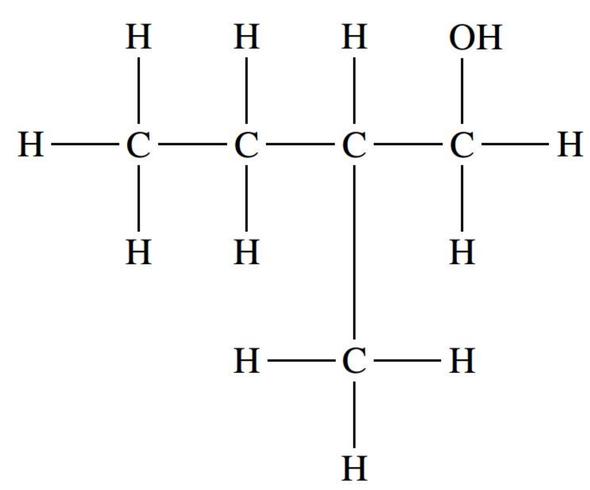
a



b



c



Continued over page

8.4 Review *continued*

d 1-fluoro-3-methylpentane
e 3-methylpentan-3-ol

6 Analyse the names of the following organic compounds and draw a structural formula for each.
a 2,2,4-trimethylhexan-3-ol
b 3-ethylpentanoic acid
c methyl butanoate

7 Consider the names of the following organic compounds. Determine whether each name provides sufficient information for you to draw a specific structure. If so, draw the structure and provide the systematic name. If not, deduce what further information is required.
a bromoethane
b dimethylpropanol

8 Analyse the names of the following organic compounds and draw a structural formula for each.
a 3-ethyl-2-methylhexanal
b propyl pentanoate
c 4-methylpentanoic acid

9 Determine why the names for each of the following organic compounds are incorrect and provide the correct names.
a 2-methylbutan-3-ol
b 3-ethylhexan-4-ol
c **2-**methylpropan-1-oic acid

10 Analyse the names of the following organic compounds and explain why each one is incorrect.
a 2-methylbutan-1-one
b pentan-3-al
c 1-methylpropanoic acid

11 Determine the systematic name for the following molecules.
a $HCOOCH_3$
b HCOOH
c $CH_3CH_2CH_2COOCH_2CH_2CH_3$
d CH_3COOCH_3
e $CH_3(CH_2)_4COOCH_2CH_3$
f $CH_3CH(CH_3)CH(CH_3)CHO$
g $CH_3COCH(CH_3)CH_2CH_3$

12 A student came across the following molecule in their reading: '2-methyl-2-iodo-3-chlorohexane'.
a Explain why this name is incorrect, according to IUPAC guidelines.
b Determine the correct name.
c Determine the condensed structural formula for this compound.

8.5 An overview of IUPAC nomenclature

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that the systematic rules for naming organic compounds are determined by the International Union of Pure and Applied Chemistry (IUPAC)
- apply the IUPAC rules to systematically name hydrocarbons, alcohols, aldehydes, ketones, carboxylic acids, haloalkanes and esters, up to C_{10}, from their structures
- draw structures for organic compounds from their systematic names.

In the early 1960s, the International Union of Pure and Applied Chemistry (IUPAC) endorsed a common naming system for carbon compounds. These rules are regularly updated and are used worldwide to enable scientists to communicate with each other. The rules ensure that a carbon compound is given a unique name that provides useful information about its structure and distinguishes it from any isomers.

The rules specify the names for different parts of an organic molecule and may include both words and numbers to indicate locations of functional groups and alkyl side chains (shown in Figure 8.5.1).

This module will summarise and extend your knowledge of the rules that you learnt in the previous modules for naming organic compounds.

IUPAC NOMENCLATURE

IUPAC nomenclature is the term used to describe the set of rules by which chemists can name a given compound. The rules can be used in reverse to determine a structure from the IUPAC name. IUPAC names of organic molecules can be short or very long but, whether simple or complex, most IUPAC names follow the same basic pattern.

Most organic molecules can be thought of as being derived from a hydrocarbon **parent molecule**, which provides the basis for the name of the molecule. Part of the IUPAC name reflects which alkane is the parent molecule.

The IUPAC name also indicates which alkyl side chains or functional groups are present in the molecule by adding a suffix to the end of the name or a prefix to the beginning of the name. The positions of alkyl side chains and functional groups are indicated by numbers, known as locants. As an example, the meaning of each part of the name 3-methylbutan-2-ol, an alcohol, is shown in Figure 8.5.2 along with its **structural formula**.

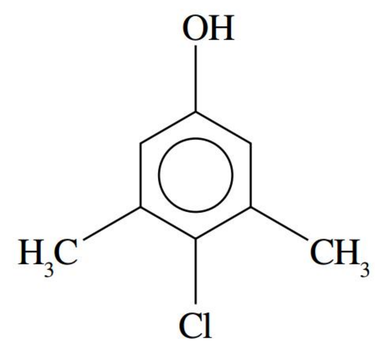


FIGURE 8.5.1 According to the IUPAC rules, the active ingredient in the antiseptic Dettol® has the name 4-chloro-3,5-dimethylphenol.

Summary of IUPAC rules for nomenclature

The following conventions are used for naming organic molecules.

- There are no spaces in a name, apart from the two-word names of esters and carboxylic acids.
- The longest carbon chain is used to derive the parent name. The longest chain must include the functional group for alkenes, alkynes, haloalkanes, alcohols, aldehydes, ketones, carboxylic acids and esters.
- The functional group is indicated in the name by adding a suffix to the end of the parent name or a prefix to the beginning of the parent name.
- The names and locations of alkyl side chains and additional functional groups are also added to this parent name.

The IUPAC name indicates the parent molecule from which the name is derived and any functional groups and alkyl side chains that are present.

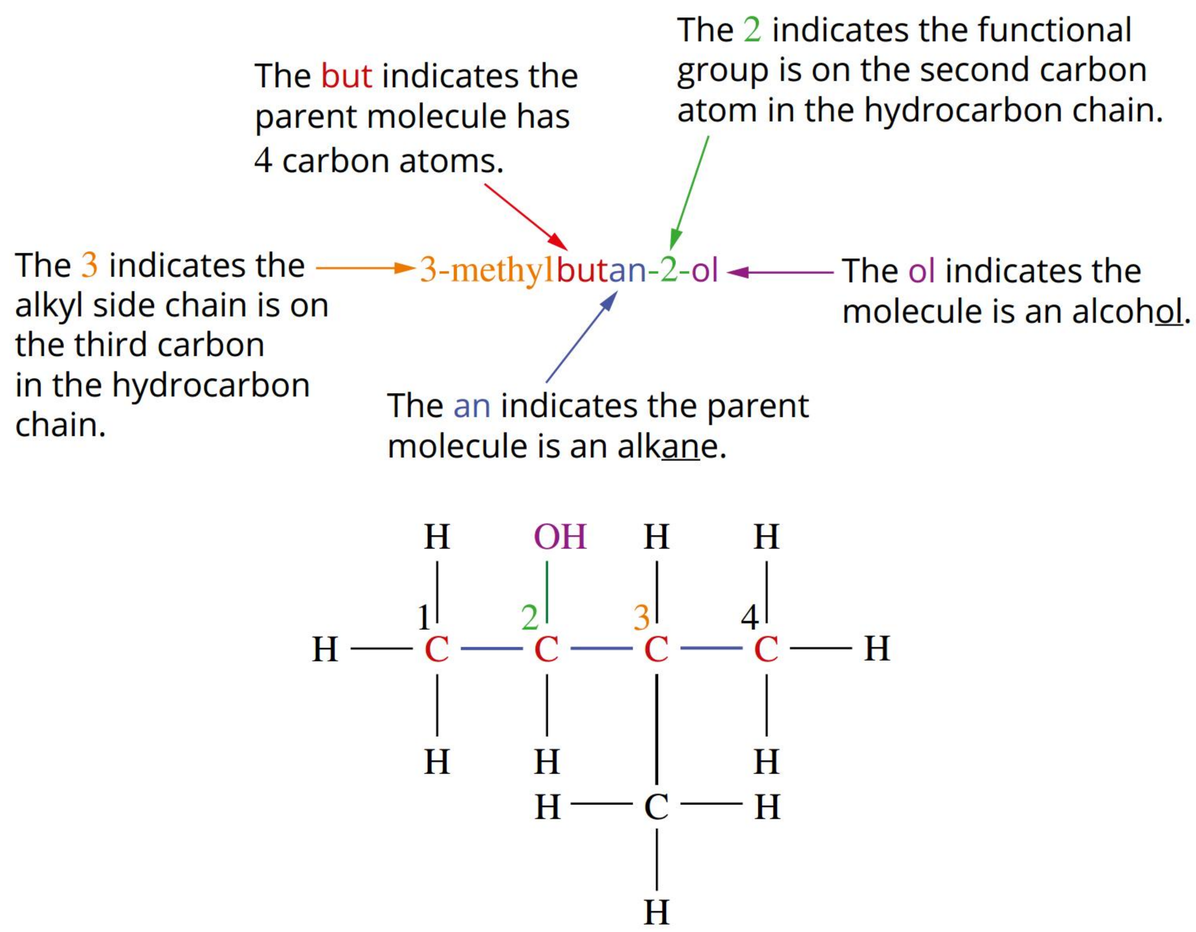


FIGURE 8.5.2 The name and extended structural formula of 3-methylbutan-2-ol. The colours of each part of the name correspond with the section of the structure that it represents.

- Locants are used to identify the carbon atom that alkyl side chains and functional groups are attached to.
- Locants and letters are separated by dashes.
- Locants are separated from other locants by commas.
- The names of alkyl side chains and additional functional groups are listed as prefixes at the beginning of a name.
- If there is more than one type of alkyl side chain or functional group to be listed at the beginning of a name, they are listed in alphabetical order.
- If there is more than one of the same type of functional group, the prefixes 'di-', 'tri-' or 'tetra-' are used. Each group is still given a locant to indicate its position on the carbon chain.

The presence of a particular functional group identifies the class a molecule belongs to and changes the molecule's name, as shown in Table 8.5.1.

TABLE 8.5.1 The identity, functional groups and naming conventions of the homologous series

Homologous series	Functional group name	Condensed structural formula	Naming convention
alkane	not applicable	not applicable	suffix '-ane'
alkene	carbon–carbon double bond	–C=C–	suffix '-ene'
alkyne	carbon–carbon triple bond	–C≡C–	suffix '-yne'
haloalkane	halo	–F, –Cl, –Br, –I	prefix 'fluoro-', 'chloro-', 'bromo-' or 'iodo-'
alcohol	hydroxyl	–OH	suffix '-ol'
amine	amino	$–NH_2$	naming not required for this course
aldehyde	carbonyl (aldehyde)	–CHO	suffix '-al'
ketone	carbonyl (ketone)	–CO–	suffix '-one'
carboxylic acid	carboxyl	–COOH	suffix '-oic acid'
ester	ester	–COO–	two-word name with suffixes '-yl' and '-oate'
amide	amide	$–CONH_2$	naming not required for this course

Omitting locants in IUPAC systematic names

Although it is common practice to omit numbers whenever a structure is unambiguous (e.g. propene instead of prop-1-ene), the IUPAC rules are not as general as this. A locant (number indicating the location of a functional group) may only be omitted in specified situations. For the molecules studied in this course:

- A locant can only be omitted if the functional group or alkyl branch is on the first carbon **and** the molecule is unambiguous.
- If one locant is needed, then all locants should be specified for that molecule.
- Locants are never used to indicate the position of a carboxyl group.

For example, the locant is omitted in the following molecules: butanoic acid, chloromethane, ethanol, pentanal and propene. Note, it is never necessary to provide a locant for carboxyl and aldehyde functional groups as these are always on the end of the molecule and therefore must be on carbon number 1.

In contrast, locants are required in 2-methylpropane and 2-methylprop-1-ene even though these structures are unambiguous without locants.

You may find these molecules commonly referred to as methylpropane and methylpropene, but these are not the correct systematic IUPAC names.

Naming organic molecules with a functional group and an alkyl side chain

Organic molecules with functional groups can also have alkyl side chains. The names of alkyl side chains are placed in alphabetical order in front of the parent name. The carbon chain is numbered from the end closest to the functional group to give the lowest possible number to the functional group.

This procedure is illustrated in Table 8.5.2 with the naming of the structural isomers of an alcohol with the molecular formula $C_4H_{10}O$.

TABLE 8.5.2 Names of isomers of an alcohol with the molecular formula $C_4H_{10}O$

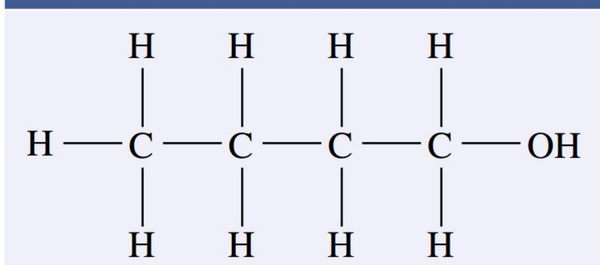
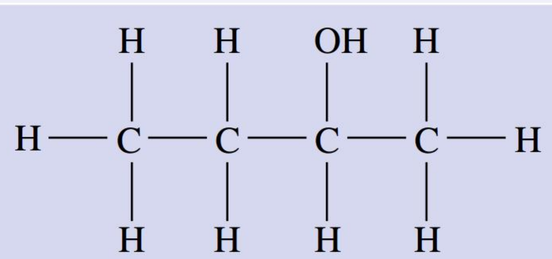
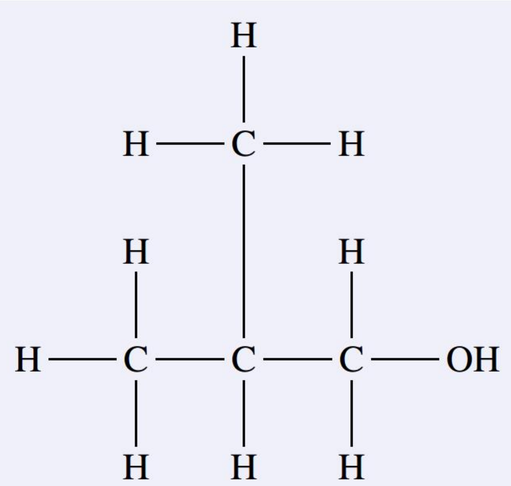
Structure	Name
	butan-1-ol
	butan-2-ol
	2-methylpropan-1-ol

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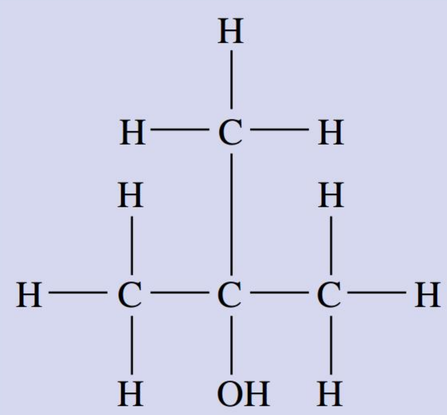
TABLE 8.5.2 *continued*

Structure	Name
	2-methylpropan-2-ol

8.5 Review

SUMMARY

- IUPAC nomenclature is a set of rules for naming an organic compound.
- The naming of organic molecules follows a series of steps.
  - Identify the longest unbranched carbon chain to determine the parent name. The longest chain must include the functional group.
  - Number the carbon chain so that the carbon attached to the highest priority functional group has the lowest number.
  - Name functional groups by prefixes or suffixes, depending on their priority.
  - Where positional isomers are possible, insert numbers (locants) before the name of each functional group. Numbers and letters are separated by dashes.
  - If there is more than one of the same type of functional group, the prefixes 'di-', 'tri-' or 'tetra-' are used. Each group is still given a number to indicate its position on the carbon chain and the numbers are separated by commas.
  - The names of alkyl side chains are added before the parent name. Each alkyl side chain is numbered to show its position on the carbon chain. If there is more than one of the same alkyl side chain, the prefixes 'di-', 'tri-' or 'tetra-' are used. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas.
  - If there is more than one type of functional group to be listed at the beginning of the name, or there is a functional group and an alkyl side chain to be listed at the beginning of the name, they are listed in alphabetical order.
  - The name is written with no spaces, apart from the two-word names of carboxylic acids and esters. Hyphens are used between numbers and words, and commas are used to separate numbers (e.g. 2,3-dichlorobutane).
  - Locants are omitted in the following situations only:
    - **a** when a functional group is attached to the first carbon, and the molecule is unambiguous (e.g. ethanol, propene)
    - **b** when a functional group can only be located on the first carbon (e.g. butanoic acid, pentanal)
    - **c** If one locant is needed in a systematic name, then all other locants should be specified (e.g. 2-methylprop-1-ene)
  - Locants are never given for carboxyl groups, even if other locants are needed in the name.
  - If geometric (*cis* and *trans*) isomers are possible (in unsaturated molecules), *prefixes cis-* or *trans-* are used to indicate the orientation of groups around the double or triple carbon–carbon bond.

KEY QUESTIONS

Describe

1 **a** State what the term 'IUPAC' stands for.

b Describe what the term 'IUPAC nomenclature' means.

2 Under what circumstances should prefixes *cis*- and *trans*- be used?

Apply

3 Depict the condensed and extended structural formulas of the functional group in each of the following classes of organic compounds.

a alkyne
b carboxylic acid
c aldehyde
d amide
e alcohol
f ester

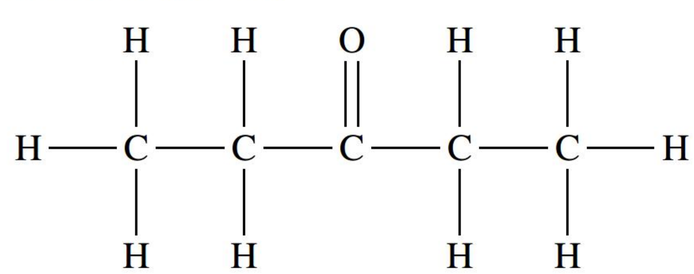
Analyse

4 Analyse the names of the following organic compounds and draw their structural formulas.

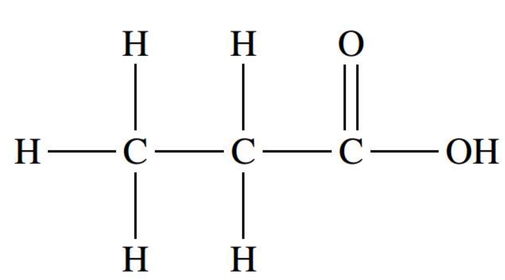
a 3-methylbutanoic acid
b 4-chlorohept-2-ene
c *trans*-3,4-dibromohept-3-ene
d *cis*-4,5-diethylnon-4-ene

5 Analyse the following molecules and determine their systematic names.

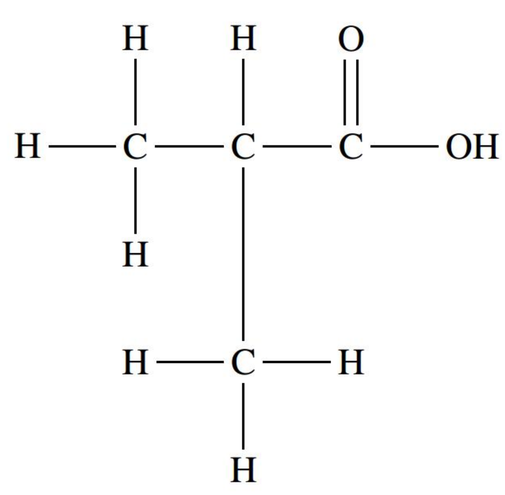
a



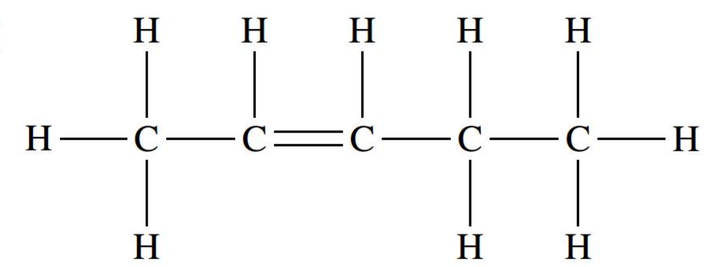
b



c

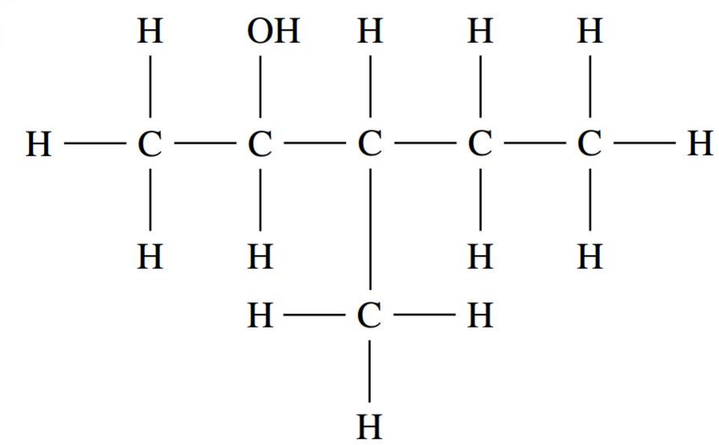


d

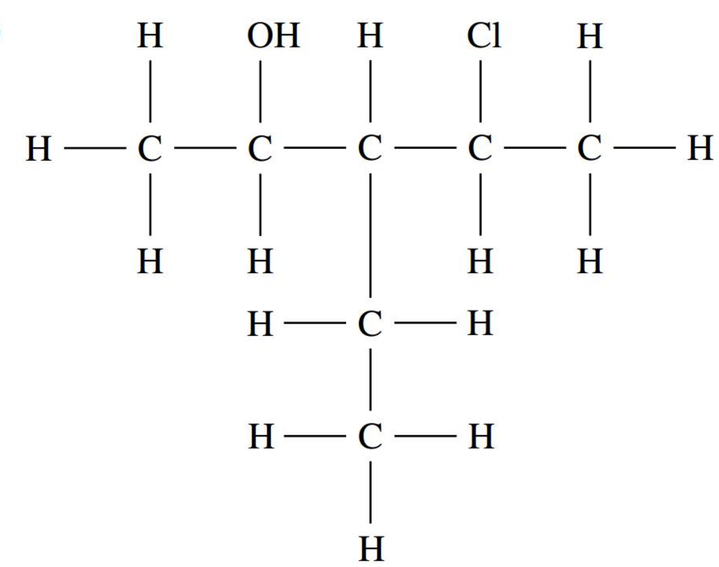


6 Analyse the following molecules and determine their systematic names.

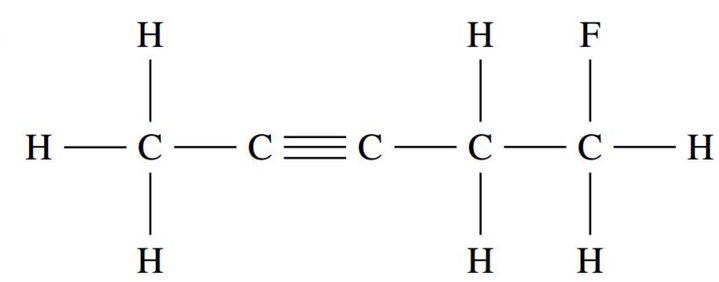
a



b



c



7 Analyse the names of the following organic compounds and draw their structural formulas.

a propan-2-ol
b 1-chlorohexane
c 2-methylbutanal
d 2,3-dimethylbutane

8.6 Trends in the melting point, boiling point and volatility of organic compounds

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that organic compounds display characteristic trends in their melting points, boiling points and volatility that are dependent on the functional groups present in their molecules
- describe how intermolecular forces influence the melting point, boiling point and volatility of organic compounds
- predict and explain the trend in melting point, boiling point and volatility for organic compounds that are members of the same homologous series
- predict and explain differences in boiling points and volatility between organic compounds from different homologous series
- predict and explain how molecular shape can influence boiling points of organic compounds
- predict and explain how the position of the functional group can influence boiling points of organic compounds.

The functional groups that are present in organic compounds are responsible for many of their chemical and physical properties. In this module and Module 8.7, you will focus on the effect that functional groups have on physical properties such as **melting point**, **boiling point**, **solubility** and **volatility**. Differences in chemical properties will be discussed in the next chapter.

Organic compounds are made up of molecules that are held together in the liquid and solid states via attractive forces known as intermolecular forces. As you will see in this module, the boiling point and volatility of an organic compound depend upon the strength of the intermolecular forces present between its molecules in the liquid state.

You will recall that homologous series are classes of organic compounds that contain the same functional group. Members of a homologous series show a steady change in many of their physical properties. In this module, you will use your knowledge of intermolecular forces to understand how and why melting point, boiling point and volatility change within homologous series.

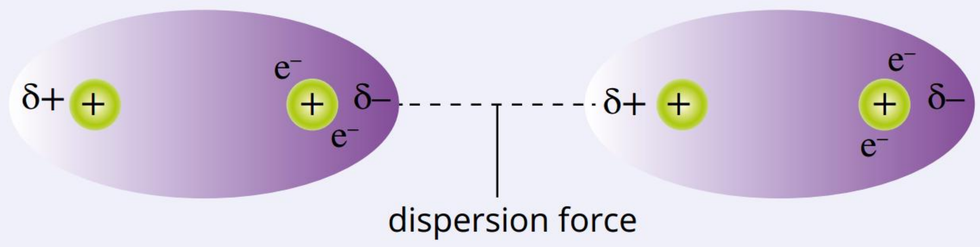
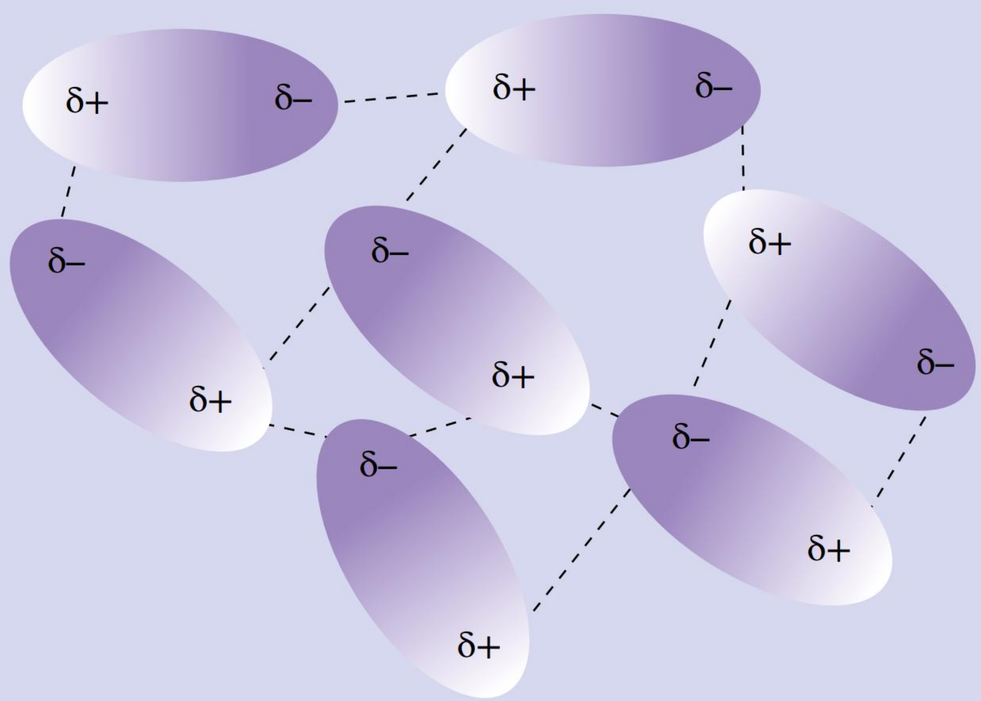
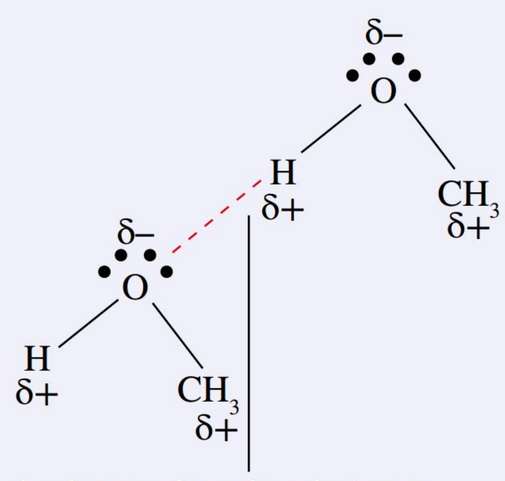
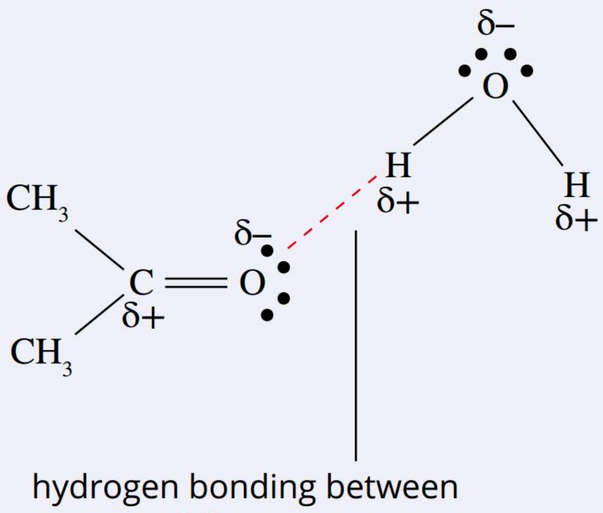
Members of different homologous series contain different functional groups and, as a result, often display very different physical properties. As you work through the module, you will use your knowledge of intermolecular forces to explain the effect of different functional groups on melting point, boiling point and volatility.

BOILING POINT

Boiling occurs when molecules in the liquid state have enough energy to completely overcome the intermolecular forces holding them together. This means that organic compounds with stronger intermolecular forces will require more energy, and therefore have higher boiling points than organic compounds with weaker intermolecular forces.

The different types of intermolecular forces and their relative strengths were introduced in Unit 2 and are summarised in Table 8.6.1.

TABLE 8.6.1 The different types of intermolecular forces

Intermolecular forces	Example	Description	Relative strength (when comparing molecules of a similar molecular mass)
dispersion forces		Dispersion forces occur between all molecules, no matter whether they are polar or non-polar. Dispersion forces are caused by **temporary dipoles** in the molecules that are the result of random movement of the electrons surrounding the molecules. When comparing molecules of the same molecular mass, dispersion forces are generally weaker than dipole–dipole forces and hydrogen bonding. When comparing molecules with similar functional groups, larger molecules and molecules with less branching will have stronger dispersion forces.	the weakest intermolecular forces
dipole–dipole forces		Dipole–dipole forces occur between polar molecules. They result from the attraction between the positive and negative ends of polar molecules.	stronger than dispersion forces but much weaker than hydrogen bonding
hydrogen bonding	 hydrogen bonding between methanol molecules  hydrogen bonding between water and the oxygen atom of propanone (acetone)	This is a particularly strong form of dipole–dipole force. For hydrogen bonding to occur, the molecules must have: a hydrogen atom covalently bonded to a nitrogen, oxygen or fluorine atom, and a non-bonding pair of electrons on the nitrogen, oxygen or fluorine atoms on neighbouring molecules. Hydrogen bonding is the strongest type of intermolecular force.	the strongest intermolecular forces

Boiling points of hydrocarbons

You learnt in Module 8.2 that alkanes and alkenes are hydrocarbons. Molecules of hydrocarbons are **non-polar**, which means that the only intermolecular forces of attraction that exist between them in the liquid state are relatively weak **dispersion forces**. Consequently, hydrocarbons generally have lower boiling points than organic compounds of a similar chain length that contain **polar** functional groups. Table 8.6.2 compares the boiling points of two hydrocarbons (butane and but-1-ene) with chlorobutane. Butane and but-1-ene both have very low boiling points; this is consistent with the fact that they are non-polar molecules and are held together in the liquid state with relatively weak dispersion forces. However, chlorobutane is a member of the haloalkane homologous series and contains a polar carbon–chlorine bond. Like the hydrocarbons, chlorobutane contains weak dispersion forces between its molecules, but the presence of the chlorine functional group also allows **dipole–dipole forces** of attraction to occur. Because the dipole–dipole forces are stronger than dispersion forces, the boiling point of chlorobutane is higher than the boiling points of butane and but-1-ene.

> Organic compounds with stronger intermolecular forces will require more energy, and therefore have higher boiling points than organic compounds with weaker intermolecular forces.

TABLE 8.6.2 A comparison of the boiling points of hydrocarbons with a haloalkane

Compound	Boiling point (°C)
butane (C_4H_{10})	−0.5
but-1-ene (C_4H_8)	−6.3
chlorobutane (C_4H_9Cl)	78.5

Boiling points within a homologous series

The boiling points of compounds within a homologous series generally increase as the length of the carbon chain increases. Table 8.6.3 lists the boiling points of the first ten members of the alkane homologous series.

> Boiling point increases as the length of the carbon chain increases because the dispersion forces acting between the molecules get stronger.

TABLE 8.6.3 Boiling points of the first ten alkanes

Alkane	Molecular formula	Boiling point (°C)
methane	CH_4	−162
ethane	C_2H_6	−89
propane	C_3H_8	−45
butane	C_4H_{10}	−0.5
pentane	C_5H_{12}	36
hexane	C_6H_{14}	69
heptane	C_7H_{16}	98
octane	C_8H_{18}	126
nonane	C_9H_{20}	150
decane	$C_{10}H_{22}$	174

You can see that the boiling points increase from methane to decane. As the carbon chain length increases, the contact surface area between the molecules also increases and the dispersion forces get stronger, as shown in Figure 8.6.1. Because the boiling points of molecular substances are determined by the strength of their intermolecular forces, the boiling points of the alkanes increase as the length of their carbon chains increases.

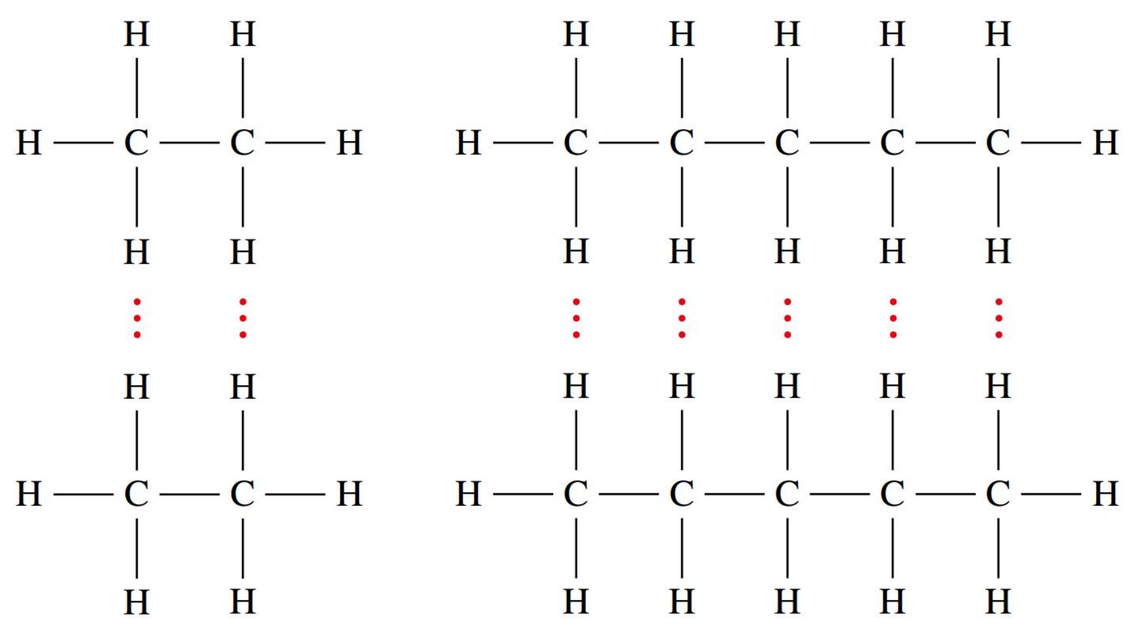


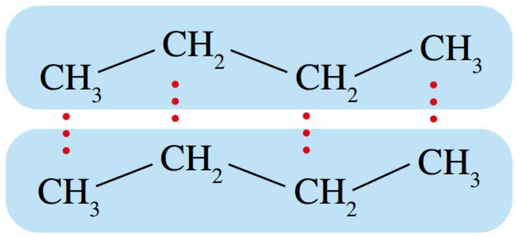
FIGURE 8.6.1 Dispersion forces are the only intermolecular forces between alkane molecules. As molecules become longer, their contact surface area increases, which results in stronger dispersion forces.

> Organic compounds made up of straight-chain molecules tend to have higher boiling points than compounds made up of branched molecules; the straight-chain molecules can fit together more closely to form stronger dispersion forces.

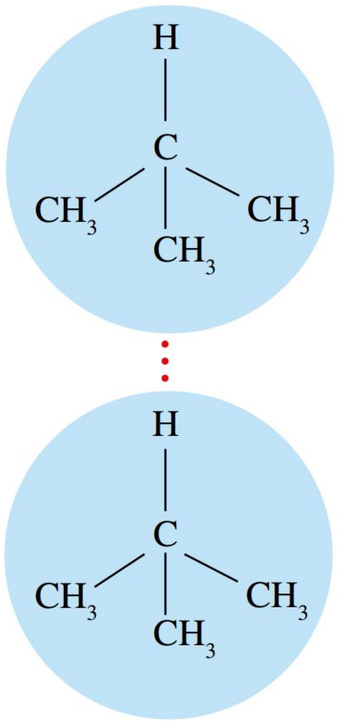
The effects of branching on boiling point

Molecular shape also influences the strength of dispersion forces and therefore boiling points. Straight-chain alkanes are able to fit together more closely and tend to have higher boiling points than their corresponding branched-chain isomers, which are unable to fit as closely together. When molecules are unable to fit closely together, the dispersion forces between them are weakened.

Figure 8.6.2 shows how the shapes of butane and its branched isomer 2-methylpropane influence the strength of the dispersion forces between their molecules. Butane ($CH_3CH_2CH_2CH_3$) boils at –0.5°C, whereas 2-methylpropane ($(CH_3)_3CH$) boils at –11.7°C. Although both molecules have the same molecular formula (C_4H_{10}), molecules of butane are more linear and can fit together more closely, allowing more contact between the molecules and therefore forming stronger dispersion forces.



butane
- more linear molecule
- molecules are closer together
- boiling point –0.5°C



2-methylpropane
- more branched molecule
- molecules are further apart
- boiling point –11.7°C

FIGURE 8.6.2 Molecular shape affects boiling point. Dispersion forces between butane molecules are stronger than those between 2-methylpropane molecules because butane molecules can fit together more closely.

Boiling points of alcohols and carboxylic acids

Hydrogen bonds are the strongest of the intermolecular forces and, as a result, molecules that can form hydrogen bonds generally exhibit higher boiling points. Molecules can form hydrogen bonds with neighbouring molecules when they contain an electronegative oxygen, nitrogen or fluorine atom attached to a hydrogen atom, and there is a lone electron pair on a nitrogen, oxygen or fluorine atom on a neighbouring molecule. This concept was discussed in detail in Unit 2. Alcohols and carboxylic acids can both form hydrogen bonds and, as shown in Table 8.6.4, they consequently have higher boiling points than alkanes of a similar molecular mass.

TABLE 8.6.4 Comparison of boiling points of compounds with different functional groups based on molecular mass

Homologous series	Compound	Formula	Molecular mass (amu)	Boiling point (°C)
alkane	butane	C_4H_{10}	58.14	–1
alcohol	propan-1-ol	C_3H_7OH	60.11	97.2
carboxylic acid	ethanoic acid	CH_3COOH	60.06	118

Boiling points of alcohols

The higher boiling points of the alcohols are due to the presence of hydrogen bonds between neighbouring alcohol molecules. In contrast, the only intermolecular forces present between non-polar alkane molecules are much weaker dispersion forces.

Oxygen is much more **electronegative** than hydrogen (it has an electronegativity value of 3.4 compared to 2.2 for hydrogen) and the oxygen–hydrogen bond in the hydroxyl functional group is a very polar bond. Figure 8.6.3 shows hydrogen bonding occurring between the partially positive hydrogen atom on one alcohol molecule and a non-bonding electron pair on the oxygen atom of a neighbouring alcohol molecule. The presence of the hydrogen bonds results in the higher boiling points observed.

> Alcohols and carboxylic acids have high boiling points because their molecules can form hydrogen bonds with neighbouring molecules; hydrogen bonds are the strongest of the intermolecular forces.

Boiling points of carboxylic acids

Hydrogen bonding also has a marked effect on the boiling points of carboxylic acids. Figure 8.6.4 shows how two molecules of a carboxylic acid in the liquid state can form **dimers** in which two hydrogen bonds occur between the molecules and results in two molecules presenting as one.

The dimer produced is a stable species that has a molecular mass double that of the single carboxylic acid molecule. The increase in size that results from the formation of the dimer also increases the strength of the dispersion forces between one dimer and its neighbours. The stronger dispersion forces combined with the hydrogen bonds between molecules result in the higher boiling points observed for carboxylic acids when compared to most other organic molecules of similar molecular masses. Table 8.6.5 highlights the higher boiling points of carboxylic acids compared to alcohols.

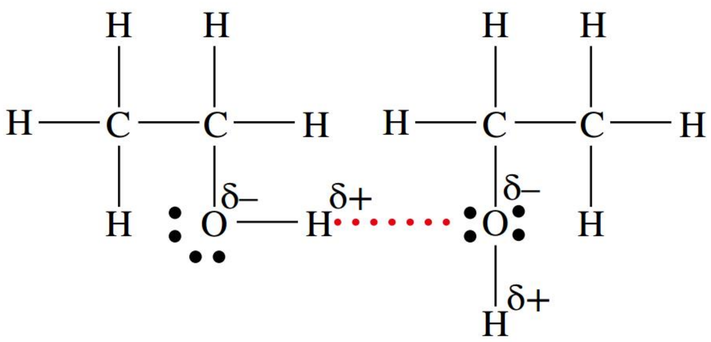


FIGURE 8.6.3 The red dotted line shows the hydrogen bond between molecules such as ethanol that contain the polar hydroxyl functional group.

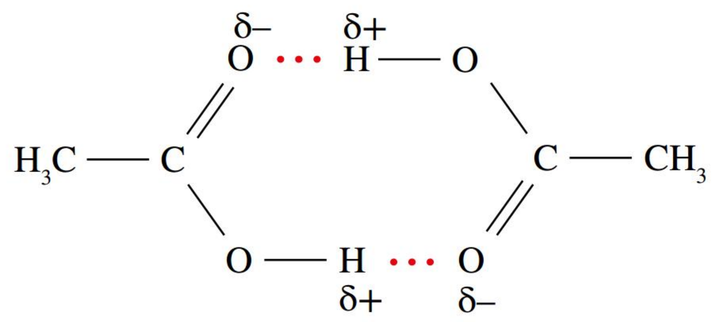


FIGURE 8.6.4 Hydrogen bonding between two ethanoic acid molecules

Carboxylic acids have particularly high boiling points due to their ability to form dimers. The dimers are stabilised by hydrogen bonds and have a molecular mass double that of a single carboxylic acid molecule. This results in stronger dispersion forces between one dimer and its neighbours.

TABLE 8.6.5 Comparison of boiling points of selected carboxylic acids with alcohols of similar molecular mass

Name	Condensed structural formula	Molecular mass (amu)	Boiling point (°C)
ethanoic acid	CH_3COOH	60.06	118
propan-1-ol	$CH_3CH_2CH_2OH$	60.11	97.2
propanoic acid	CH_3CH_2COOH	74.09	141
butan-1-ol	$CH_3(CH_2)_2CH_2OH$	74.14	117
butanoic acid	$CH_3(CH_2)_2COOH$	88.12	164
pentan-1-ol	$CH_3(CH_2)_3CH_2OH$	88.17	138

Boiling points within the homologous series

The boiling points of alcohols and carboxylic acids increase as molecular mass increases. Just as we have seen for the homologous series discussed earlier, as the size of molecules increases, dispersion forces get stronger; this results in higher boiling points. Figure 8.6.5 shows the increase in boiling points within the homologous series of alcohols and carboxylic acids.

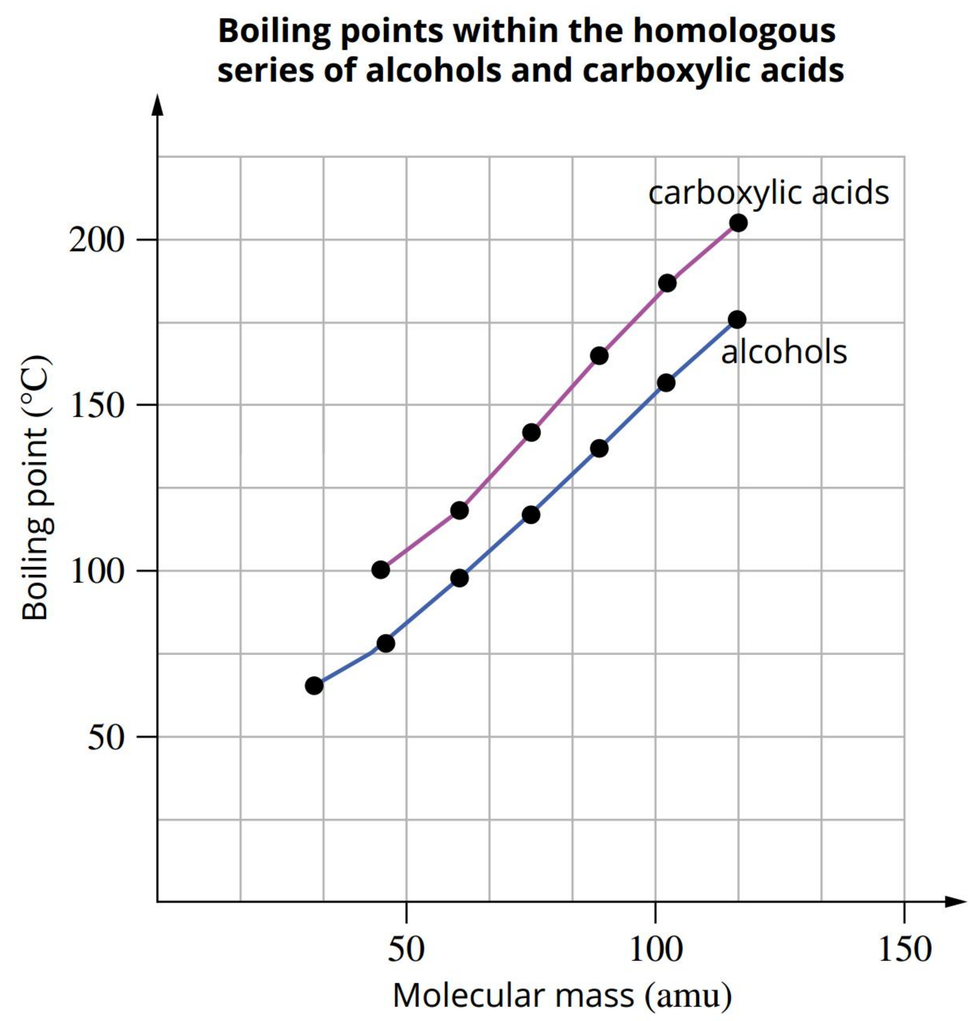


FIGURE 8.6.5 Boiling points of the alcohol and carboxylic acid homologous series with increasing molecular mass. The boiling points of carboxylic acids are higher than the boiling points of alcohols because of their ability to form dimers, which are stabilised by hydrogen bonds between the molecules.

The effects of branching on boiling point

In the earlier discussion on the boiling points of alkanes, we saw that branched-chain isomers generally have lower boiling points than straight-chain alkanes because their molecules cannot fit as closely together, resulting in weaker dispersion forces. In the case of molecules with functional groups, in addition to the impact of branching on the strength of dispersion forces, other intermolecular forces can also be affected.

For example, in alcohols, the position of the hydroxyl group affects the hydrogen bonding. Figure 8.6.6 shows molecular models for three isomers of butanol: butan-1-ol, butan-2-ol and 2-methylpropan-2-ol. These isomers are examples of primary, secondary and tertiary alcohols, respectively.

As shown in Table 8.6.6, the boiling points of these alcohols decrease in the sequence from primary to secondary to tertiary alcohol. This is because the hydroxyl group becomes increasingly 'crowded' moving from the primary through to the secondary and tertiary isomers; the alkyl groups restrict the molecule's ability to form hydrogen bonds with other molecules.

TABLE 8.6.6 The boiling points of primary, secondary and tertiary alcohols with the formula C_4H_9OH

Alcohol	Type of alcohol	Boiling point (°C)
butan-1-ol	primary	118
butan-2-ol	secondary	100
2-methylpropan-2-ol	tertiary	82

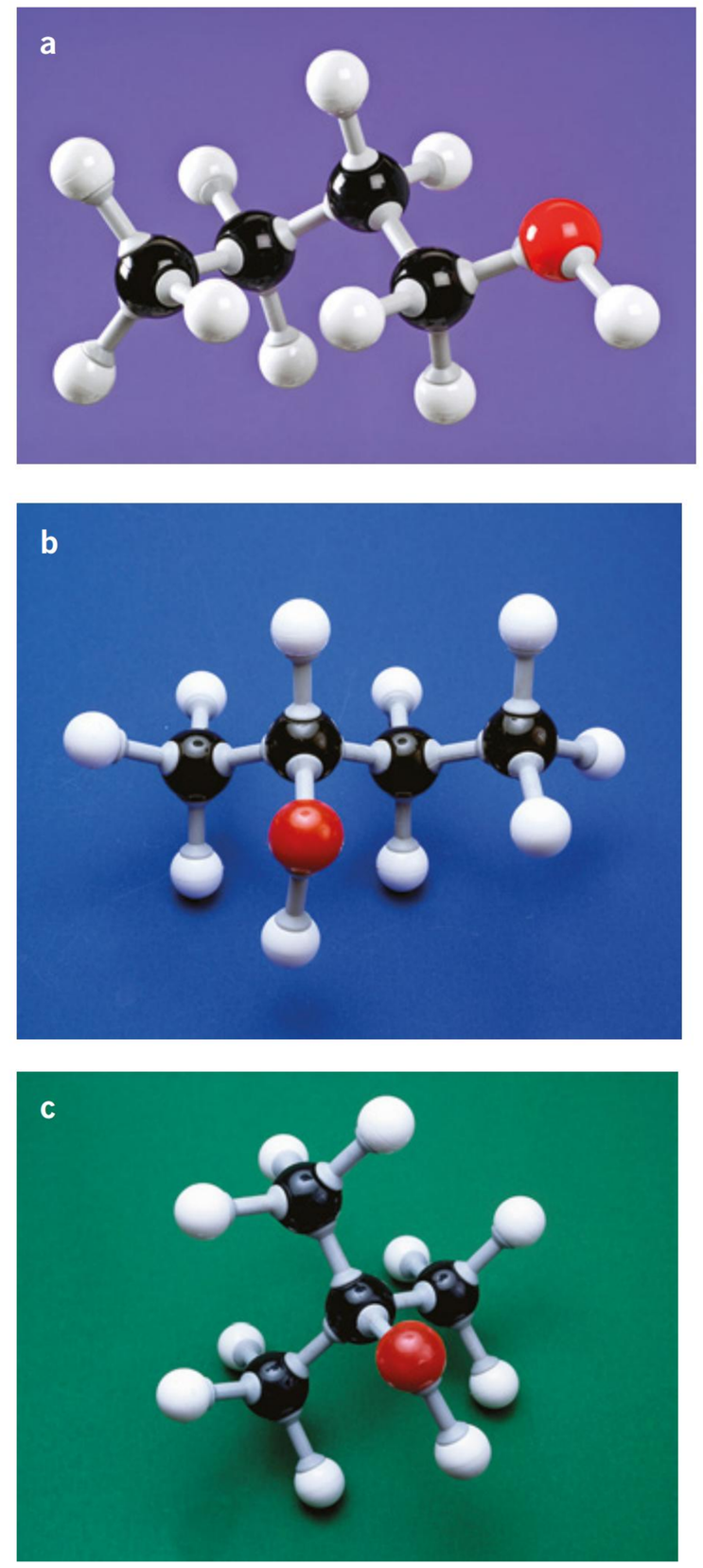


FIGURE 8.6.6 Molecular models of the three isomers of butanol: (a) butan-1-ol, (b) butan-2-ol and (c) 2-methylpropan-2-ol.

Worked example 8.6.1

PREDICTING WHICH ORGANIC COMPOUND HAS THE HIGHEST BOILING POINT

In each of the following sets of compounds, predict which one would have the highest boiling point.

a butan-1-ol, hexan-1-ol, pentan-1-ol

b pentan-1-ol, 2-methylbutan-1-ol, 2-methylbutan-2-ol

Thinking	Working
Compare the compounds in each set and identify any relationship between them.	**a** All three compounds are members of the alcohol homologous series. They increase in carbon chain length as follows: butan-1-ol < pentan-1-ol < hexan-1-ol **b** All three compounds are structural isomers of each other.
a Determine how the boiling points change within a homologous series.	**a** Boiling points increase within a homologous series. As the carbon chain length increases in size, the strength of the dispersion forces also increases and results in progressively higher boiling points.
b Determine how branched isomers and the position of the functional group affects boiling point.	**b** Branched isomers generally have lower boiling points than straight-chain compounds for two reasons. Firstly, the dispersion forces between branched molecules are weaker than those between straight-chain molecules. Secondly, intermolecular forces formed between functional groups on neighbouring branched molecules are weaker than those formed between straight-chain molecules. This is because the surrounding alkyl groups on the branched molecules 'crowd' the functional groups and restrict their ability to form effective intermolecular forces with neighbouring molecules.

Using your understanding from above, determine which compound in each set has the highest boiling point.	**a** Hexan-1-ol has the longest carbon chain and therefore has the highest boiling point. **b** Pentan-1-ol has the highest boiling point. It is a straight-chain isomer, so its molecules can fit together closely and form strong hydrogen bonds. The other two compounds are branched isomers; their alkyl groups crowd the hydroxyl functional groups and restrict the formation of hydrogen bonds between neighbouring molecules.

➤ Try yourself 8.6.1

PREDICTING WHICH ORGANIC COMPOUND HAS THE HIGHEST BOILING POINT

In each of the following sets of compounds, predict which one would have the highest boiling point.

a pentane, decane, octane

b 2-methylpropan-2-ol, propanoic acid, butan-1-ol

MELTING POINT

Melting occurs when molecules in the solid state have enough energy to overcome the intermolecular forces holding them in place. This means that organic compounds with stronger intermolecular forces will require more energy, and therefore have higher melting points than organic compounds with weaker intermolecular forces.

Similarly to the observed increase in boiling point with increasing molecular mass, the melting point within a homologous series generally increases with increasing number of carbons in the chain. However, the increase is not as regular as with the boiling point trend. For instance, in the melting points of the alkane series, shown in Table 8.6.7, the melting point of propane (–188°C) is lower than the melting point of both methane (–182°C) and ethane (–183°C).

TABLE 8.6.7 Melting points of the first ten straight-chain alkanes

Molecule	Formula	Molecular mass (amu)	Melting point (°C)
methane	CH_4	16.05	–182.4
ethane	C_2H_6	30.08	–182.8
propane	C_3H_8	44.11	–187.6
butane	C_4H_{10}	58.14	–138.2
pentane	C_5H_{12}	72.17	–129.7
hexane	C_6H_{14}	86.20	–95.3
heptane	C_7H_{16}	100.23	–90.6
octane	C_8H_{18}	114.26	–58.8
nonane	C_9H_{20}	128.29	–53.5
decane	$C_{10}H_{22}$	142.32	–29.6

As with the homologous series of alkanes, the alcohols, shown in Table 8.6.8, also show an increasing melting point as the number of carbons in the chain increases. However, as with the alkanes, the first three alcohols do not fit the trend perfectly.

TABLE 8.6.8 Melting points of the first eight straight-chain primary alcohols

Molecule	Formula	Molecular mass (amu)	Melting point (°C)
methanol	CH_3OH	32.05	–97.6
ethanol	C_2H_5OH	46.08	–114.1
1-propanol	C_3H_7OH	60.11	–126.1
1-butanol	C_4H_9OH	74.14	–89.8
1-pentanol	$C_5H_{11}OH$	88.17	–78.9
1-hexanol	$C_6H_{13}OH$	102.20	–44.6
1-heptanol	$C_7H_{15}OH$	116.23	–34.0
1-octanol	$C_8H_{17}OH$	130.26	–15.5

VOLATILITY

Organic compounds that are liquids at room temperature are described as being volatile if they evaporate easily; this means that the liquid readily forms a **vapour**. We can often detect volatile organic compounds by their smell. For example, perfumes and air fresheners contain esters that give off a pleasant smell. Nail varnish remover often contains propan-2-one (acetone), which has a very pungent smell. Many volatile organic compounds give off vapours that can be harmful to our health, so it is important to be aware of the hazards associated with using them.

The volatility of an organic compound depends upon the strength of its intermolecular forces in the liquid state. A volatile organic compound contains weak intermolecular forces of attraction, which are easily overcome, so the liquid readily evaporates. The process of evaporation is different to boiling because evaporation can occur across a range of temperatures, whereas boiling occurs at one specific temperature. However, the boiling point of a compound and its volatility are directly related. Compounds with low boiling points contain weaker intermolecular forces and are therefore more volatile than compounds with higher boiling points, which contain stronger intermolecular forces.

Volatility is also related to **vapour pressure**. Recall that the vapour pressure of a liquid is the pressure exerted by a vapour in equilibrium with its liquid in a closed container (this was discussed in detail in Chapter 11 of *Pearson Chemistry Queensland Units 1 & 2 Student Book*). Volatile compounds evaporate more readily and therefore have a higher vapour pressure than non-volatile compounds.

Organic compounds that contain weaker intermolecular forces evaporate more easily and are therefore more volatile than organic compounds that contain stronger intermolecular forces.

Volatility of hydrocarbons

As discussed earlier in the module, hydrocarbons are non-polar and can only form dispersion forces between molecules. Small hydrocarbons that are liquids at room temperature are held together with relatively weak dispersion forces; consequently, they are highly volatile and have low boiling points. As the length of the carbon chain increases within a homologous series, the dispersion forces get stronger resulting in the compounds, becoming less volatile and having higher boiling points. Consider the first ten members of the homologous series of alkanes. As shown in Table 8.6.3, the boiling points increase as the carbon chain increases in length. Methane, ethane, propane and butane are gases at room temperature and therefore are not described in terms of volatility, but pentane to decane are liquids; these liquid alkanes range from being highly volatile to volatile and then semi-volatile, depending on the length of their carbon chain.

Volatility of alcohols and carboxylic acids

Alcohols and carboxylic acids are much less volatile and have higher boiling points than hydrocarbons of a similar chain length; this can be seen in Table 8.6.9. The lower volatility and higher boiling points of alcohols and carboxylic acids are due

to the relatively strong hydrogen bonding that exists between their molecules in the liquid state. Carboxylic acids are the least volatile out of the two classes because, as discussed earlier, they form dimers, which effectively double their molecular mass and increase the strength of the dispersion forces acting between their molecules.

TABLE 8.6.9 Comparison of boiling points of alcohols and carboxylic acids with an alkane

Homologous series	Compound	Formula	Boiling point (°C)
alkane	butane	C_4H_{10}	−0.5
alcohol	butan-1-ol	$C_4H_{10}O$	118
carboxylic acid	butanoic acid	$C_4H_8O_2$	164

As seen with the other classes of organic compounds, when the carbon chain length of the compounds increases, volatility decreases due to the dispersion forces becoming stronger.

8.6 Review

SUMMARY

- The melting and boiling points of organic molecules are determined by the strength of the intermolecular forces. Dispersion forces are always present and there may also be dipole–dipole forces or hydrogen bonds.
- The only forces of attraction between molecules of the alkane and alkene homologous series are dispersion forces.
- Molecules of alcohols and carboxylic acids contain functional groups that can form hydrogen bonds with other molecules.
- When comparing molecules of a similar molecular mass in different homologous series, it is generally true that their melting points and boiling points increase in the following order: alkanes < alkenes < alcohols < carboxylic acids.
- The strength of dispersion forces between molecules depends on both the size and shape of the molecules.
- When comparing molecules from the same homologous series, both melting and boiling points increase as the carbon chain length increases. This is because the longer carbon chains can form stronger dispersion forces between neighbouring molecules.
- Straight-chain molecules are able to fit together more closely and tend to have higher boiling points than their corresponding branched-chain isomers, which are unable to fit as closely together. This is because dispersion forces are weakened when molecules are further apart.
- The position of functional groups within molecules can also affect melting and boiling points. If surrounding alkyl groups prevent functional groups between neighbouring molecules from approaching each other closely enough, then the intermolecular forces formed between them will not be as effective and will result in lower melting and boiling points.
- Organic compounds that are liquids at room temperature are described as being volatile if they evaporate easily. Small hydrocarbons that are liquids at room temperature are highly volatile because their molecules are held together with only relatively weak dispersion forces.
- Organic compounds that contain stronger intermolecular forces of attraction tend to be less volatile.
- Alcohols and carboxylic acids are much less volatile than hydrocarbons of a similar molecular mass due to the relatively strong hydrogen bonding that exists between their molecules.
- For all organic compounds, as their carbon chain length increases, their volatility, melting and boiling points all decrease because the dispersion forces between their molecules become stronger.

KEY QUESTIONS

Describe

1 Recall the intermolecular forces of attraction that exist between molecules of alkanes and alkenes.

2 Describe what is meant when a liquid is described as being volatile.

Apply

3 Construct a diagram that shows the hydrogen bonding that exists in the liquid state between molecules of ethanol.

4 Explain why a small, non-polar organic compound like pentane is volatile.

5 Identify and explain the two factors that affect the strength of dispersion forces between molecules.

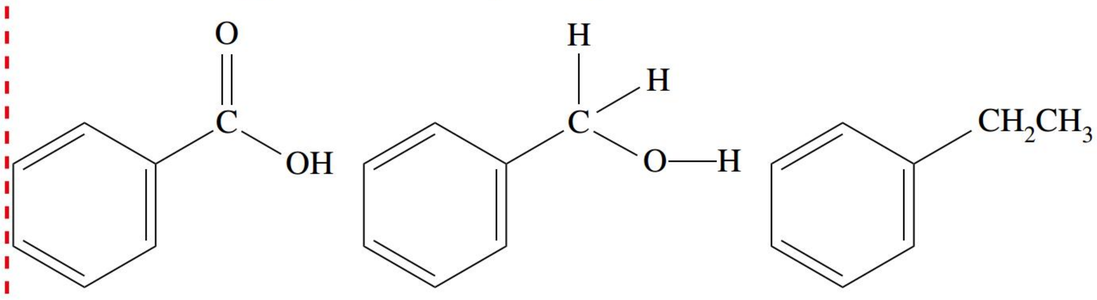
6 Identify the functional groups that can form dipole-dipole forces between molecules.

7 Identify the functional groups that can form hydrogen bonds between molecules.

Analyse

8 Pentane, 2-methylbutane and 2,2-dimethylpropane are structural isomers with a molecular formula of C_5H_{12}. Rank these compounds in order of increasing boiling point. Explain your order.

9 Analyse the structural formulas of the three organic compounds below. Classify them in order of increasing boiling point, and explain your order.



compound 1 compound 2 compound 3

10 The following compounds are liquids at room temperature and have a similar molecular mass. Classify them in order of increasing volatility and explain your order.
butan-1-ol, pentane, butanoic acid

11 Classify the following alkanes in order of increasing volatility and explain your order.
hexane, octane, decane

12 The table below shows the results obtained in a series of experiments to determine the boiling points of various organic compounds.

Experiment	Organic compound	Molecular mass (amu)	Boiling point (°C)
1	CH_3CH_2OH	46.08	78.0
	HCOOH	46.03	102
2	$CH_3(CH_2)_2CH_2OH$	74.14	119
	CH_3CH_2COOH	74.09	139
3	$CH_3(CH_2)_4CH_2OH$	102.20	157
	$CH_3(CH_2)_3COOH$	102.15	152

a Analyse the data and draw conclusions about the boiling points of these organic compounds.

b Identify any anomalies in the results (i.e. identify any results that you would not expect; these results may be due to an experimental error).

c Explain your answers to parts **a** and **b**.

13 An ester can be made via the reaction of an alcohol with a carboxylic acid. The process is called esterification. Because the reaction does not go to completion, there is always an equilibrium mixture of reactants and products at the end. The esters can be purified by refluxing and distilling the components of each reaction mixture. The following table shows the boiling points of the reactants and products of several esterification reactions.

Alcohol	Boiling point (°C)	Carboxylic acid	Boiling point (°C)	Ester	Boiling point (°C)
methanol	64.5	methanoic acid	101	methyl methanoate	31.5
ethanol	78.5	propanoic acid	141	ethyl propanoate	99.1
butan-1-ol	117	ethanoic acid	118	butyl ethanoate	126

Analyse the data in the table and identify the ester whose purification process would:

a result in it being the first component collected in the distillation process

b result in it being the last component collected in the distillation process

c be the most difficult to distinguish between the three components in the distillation process.

Continued over page

8.6 Review *continued*

14 Vapour pressure can be used as a measure of an organic compound's volatility. A highly volatile compound will have a high vapour pressure. A less volatile compound will have a lower vapour pressure. Consider the vapour pressures (in kilopascals, kPa) for four organic compounds listed as A, B C and D in the table below.

Compound	Vapour pressure (kPa)
A	3850
B	214
C	68.4
D	6.11

a Classify the compounds in order of increasing volatility.

b In no particular order, the four organic compounds are pentane, ethane, butane and heptane. Determine which letter matches each compound in the table. Explain your answer.

c Predict how the volatility of ethanol would compare with the volatility of the compounds listed in the table.

d Using your understanding of the relationship between vapour pressure and volatility, predict how the vapour pressure of ethanol would compare with the vapour pressures of the alkanes listed in the table.

8.7 Solubility of organic compounds

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- describe how intermolecular forces influence the solubility of organic compounds
- predict and explain the trend in solubility (in both water and non-polar solvents) for organic compounds that are members of the same homologous series
- predict and explain differences in solubility (in both water and non-polar solvents) between organic compounds from different homologous series.

In the previous module, you learnt that members of a homologous series of organic compounds show a steady change in their melting points, boiling points and volatility, which is reflective of the strength of the dispersion forces between their molecules. You also learnt that members of different homologous series often display very different melting and boiling points and vary in their volatility because their molecules are held together by different intermolecular forces. In this module, you will focus on one more physical property, solubility. Just as you observed for melting point, boiling point and volatility, you will see that the trends observed for solubility, both within the same homologous series and across different homologous series, are dependent on the strength of the intermolecular forces that can be formed.

SOLUBILITY

The intermolecular forces present in an organic compound have an important effect on its solubility. The different types of intermolecular forces and their relative strengths were covered in Unit 2. Recall that dispersion forces are generally the weakest intermolecular forces; while they are present between all molecules, they are the only intermolecular forces that exist between non-polar molecules. Dipole–dipole forces are stronger than dispersion forces and occur between polar molecules. Hydrogen bonds are the strongest intermolecular forces and only occur between highly polar molecules in which a hydrogen atom is covalently bonded to an oxygen, a nitrogen or a fluorine atom. Due to the difference in electronegativity between the atoms involved, the hydrogen develops a partial positive charge and is attracted to a lone electron pair on an oxygen, a nitrogen or a fluorine atom on an adjacent molecule.

In general, a solute will dissolve in a **solvent** that has similar intermolecular forces. In the first step of the dissolving process, energy is required to break the intermolecular forces in both the pure solute and pure solvent. Energy is then released when new intermolecular forces form between the solute and solvent. A solute will only dissolve in a solvent if the energy released in the formation of the new solute–solvent intermolecular forces is greater than the energy required to break the solute–solute and solvent–solvent intermolecular forces in the first place.

Many organic compounds are **insoluble** in water and, when mixed together, form two visible layers, such as when oil is mixed with water (Figure 8.7.1). The solubility of an organic compound in water is dependent on two main factors, namely any functional groups present in the compound (due to their interaction with water molecules) and the length of the hydrocarbon portion of the molecule. These factors determine the strength of the intermolecular forces that can be formed with the water molecules, which in turn determines whether the compound will be soluble.

FIGURE 8.7.1 When oil is mixed with water, two visible layers are formed with the oil floating on top of the water.

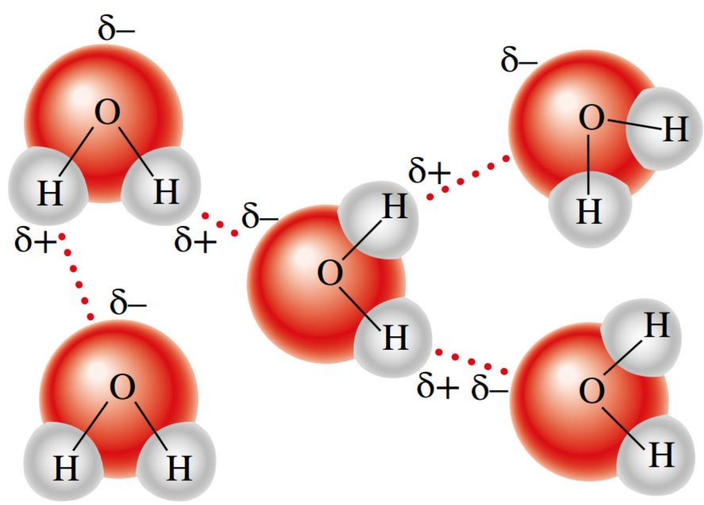


FIGURE 8.7.2 Water molecules are held together by hydrogen bonds.

> In general, a solute will dissolve in a solvent if it has similar intermolecular forces.

As shown in Figure 8.7.2, water molecules are polar and are held together by hydrogen bonds, which are particularly strong intermolecular forces of attraction. When solutes dissolve in water, a relatively large amount of energy is required to break these hydrogen bonds between the water molecules. Organic compounds are therefore more likely to dissolve if their functional groups are able to form similar hydrogen bonds with the water molecules; this is because the energy released when the new hydrogen bonds form compensates for the energy required when the hydrogen bonds between the water molecules are broken in the first place.

Solubility of hydrocarbons

The non-polar nature of alkanes and alkenes makes them insoluble in water. If they were to dissolve, they could only form weak dispersion forces with the water molecules. The energy released on the formation of these dispersion forces would not be enough to compensate for the much larger amount of energy that would be required to break the hydrogen bonds between the water molecules in the first place. As a result, the two substances remain separate and do not mix. For example, when hexane is added to water, it simply forms a layer on top of the water; the two liquids do not mix and the hexane floats on top of the water because it is less dense than water. Liquids that do not mix are said to be **immiscible**.

Crude oil is a mixture of many different compounds. Most of these compounds are hydrocarbon compounds of varying lengths. While there are some alkenes in crude oil, many of the hydrocarbons are alkanes. Because alkanes are generally less dense than water, when crude oil spills occur at sea, the crude oil floats on the surface, forming a thick insoluble layer. As the oil layer is moved by the waves of the sea, the oil can spread over many hundreds of square kilometres. The presence of the thick oil layer can have disastrous consequences for marine and bird life. Oil that reaches the shore, like the oil spill shown in Figure 8.7.3, has catastrophic effects on beaches and wildlife.

FIGURE 8.7.3 Oil spills at sea can contaminate shorelines and are very difficult to clean due to the lack of solubility of the oil in the water. Other non-polar solvents or physical methods are required to disperse or remove the oil.

Solubility of hydrocarbons in organic solvents

Hydrocarbons readily dissolve in non-polar solvents such as other hydrocarbons or symmetrical haloalkanes (e.g. pentane is soluble in octane and tetrachloromethane). This is because the energy required to break the relatively weak dispersion forces between the solvent molecules is low and similar to the energy released when solute–solvent molecules interact. Figure 8.7.4 depicts the process of pentane dissolving in octane. Both are non-polar liquids and only contain dispersion forces; they mix easily because of their similar intermolecular forces. The energy that is required to break the pentane–pentane and octane–octane dispersion forces in the pure

liquids is compensated for by the similar amount of energy that is released when the new pentane–octane dispersion forces form. The liquids are described as being **miscible**; that is, they are soluble in each other.

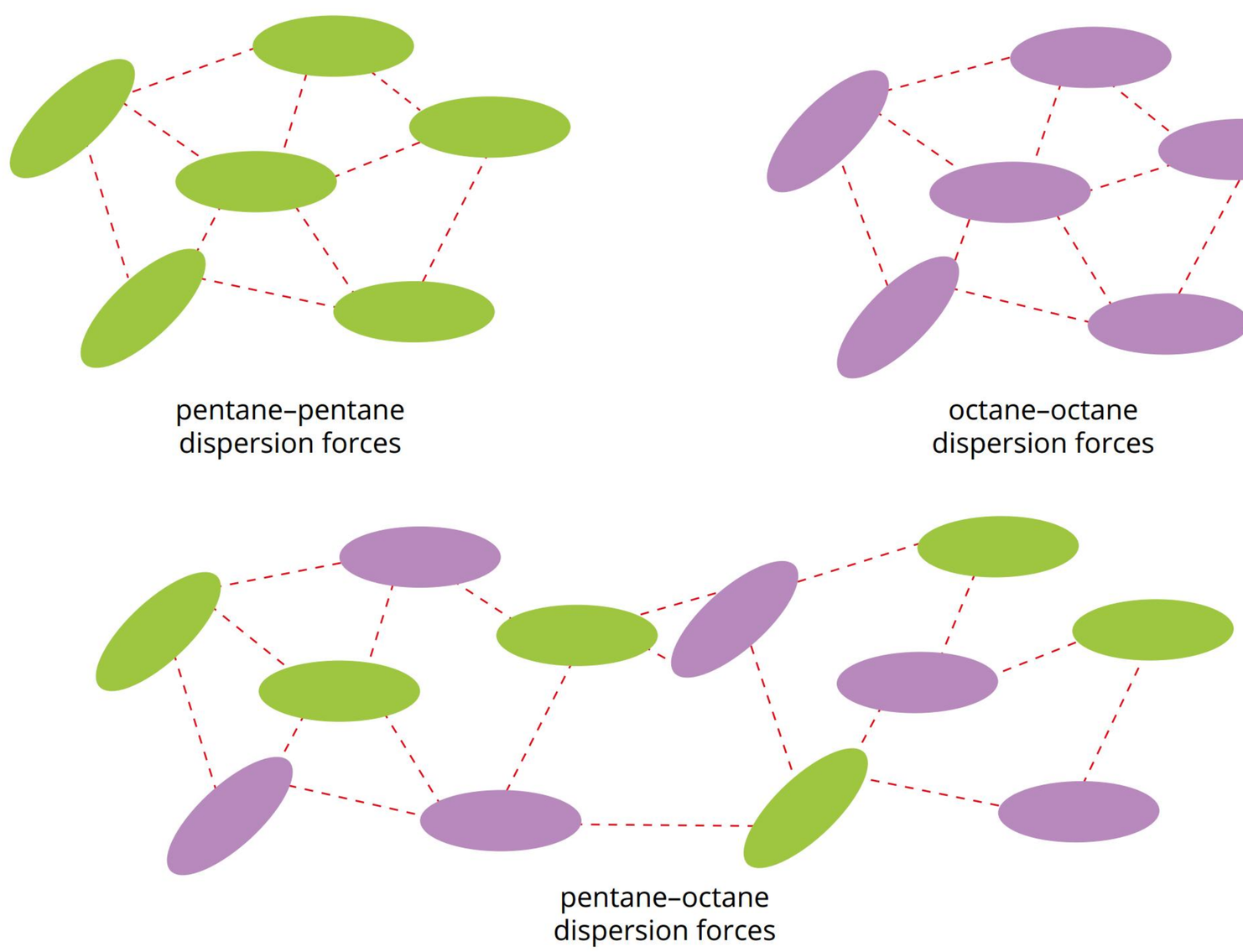


FIGURE 8.7.4 Pentane dissolves in octane. Both molecules are non-polar and are attracted to each other by dispersion forces.

Many commercial cleaning agents contain non-polar liquids that are useful for removing oil stains. White spirit is a mixture of alkanes and other hydrocarbons obtained by the refining of crude oil. White spirit is a useful cleaning agent because it can dissolve other non-polar liquids, such as oils and greases. It is used as a solvent in aerosols and in the home as a degreasing solvent. White spirit is also used for cleaning paintbrushes and as a general cleaning agent (Figure 8.7.5).

FIGURE 8.7.5 White spirit contains a mixture of alkanes. It is a useful solvent for other non-polar liquids.

Solubility of alcohols and carboxylic acids

Small alcohols and carboxylic acids dissolve well in water because hydrogen bonds can form between the polar functional groups of their molecules and adjacent water molecules. While the energy required to break the hydrogen bonds in the pure solute (alcohol or carboxylic acid) and pure solvent (water) is relatively large, the release of energy when new hydrogen bonds form between the solute and solvent compensates for this; as a result, small alcohols and carboxylic acids are highly soluble in water.

As depicted in Figure 8.7.6a, when alcohols dissolve in water, hydrogen bonds form between the partially positive hydrogen atoms of the hydroxyl groups (–OH) and the lone pairs of electrons on the oxygen atoms of adjacent water molecules. There is also attraction between the partially positive hydrogen atoms within water molecules and the lone pairs of electrons on the hydroxyl groups of the alcohol molecules. This is how ethanol dissolves in water in alcoholic drinks, such as beer and wine.

When carboxylic acids dissolve in water, hydrogen bonding occurs between water molecules and both the C=O group and the –OH group, making these compounds more soluble than alcohols in water; this is depicted in Figure 8.7.6b.

As you will recall from Module 3.2, carboxylic acids are also weak acids that partially ionise in water, further increasing their solubility, e.g.:

$$CH_3COOH(l) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Hydrocarbons are insoluble in polar solvents such as water, but soluble in non-polar solvents such as other hydrocarbons or symmetrical haloalkanes.

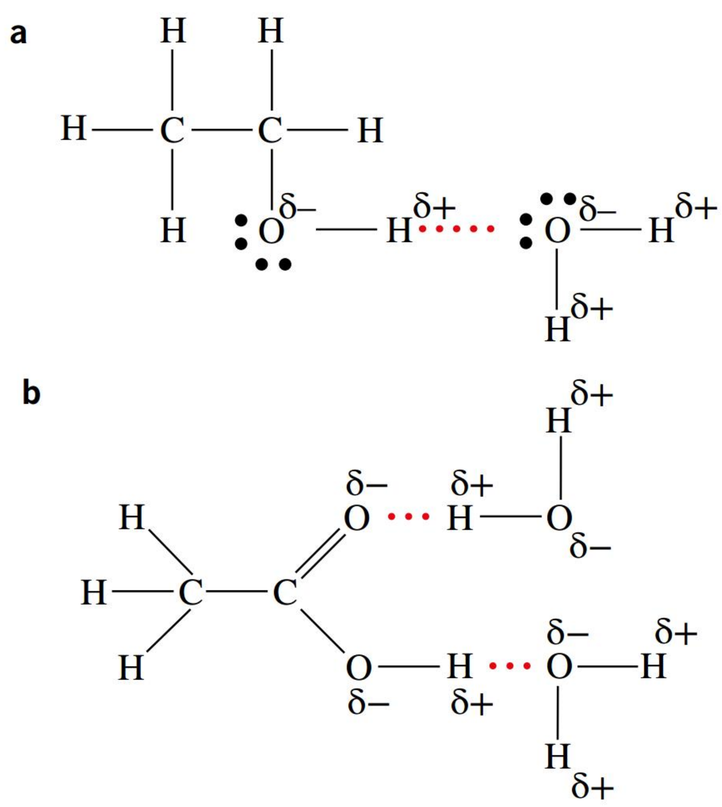


FIGURE 8.7.6 (a) Hydrogen bonding between water molecules and an ethanol molecule. (b) Carboxylic acids are more soluble in water than alcohols because hydrogen bonding occurs between the water molecules and both the carbonyl group (C=O) and the hydroxyl group (–OH).

Figure 8.7.7 shows how the polar water molecules surround the newly formed ions and ion–dipole attractions and hydrogen bonds form.

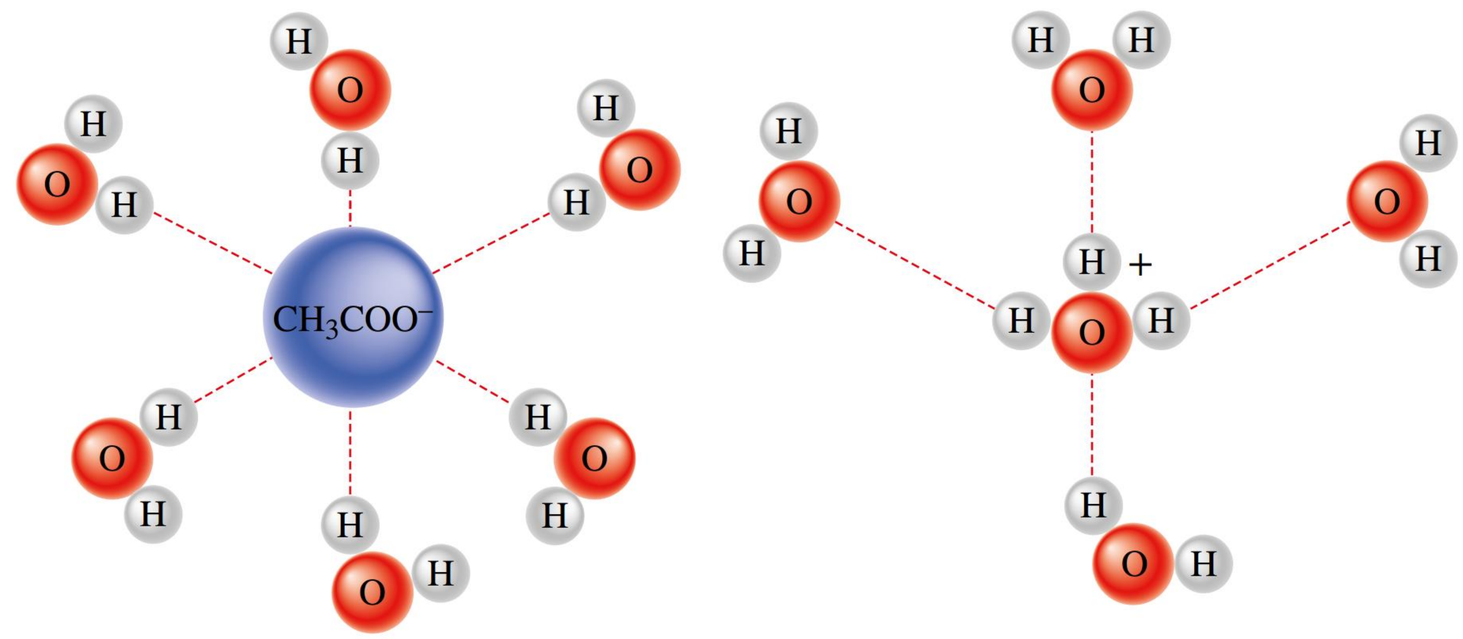


FIGURE 8.7.7 When ethanoic acid molecules (CH_3COOH) ionise in water, the newly formed ions are surrounded by adjacent water molecules. The polar water molecules form ion–dipole attractions with the ethanoate ions (CH_3COO^-) and hydrogen bonds with the hydronium ions (H_3O^+). These intermolecular forces are represented in the diagram by dashed lines.

Solubility within a homologous series

The smaller alcohols, methanol and ethanol, dissolve readily in water. As the carbon chain increases in length and the alcohols get bigger, their solubility in water decreases. This is because the alcohol's non-polar hydrocarbon 'tail' gets longer, reducing the amount of hydrogen bonding that can occur between the hydroxyl group and water molecules, so the alcohols become less soluble. Figure 8.7.8 shows the solubility of three alcohols decreasing as their carbon chain length increases.

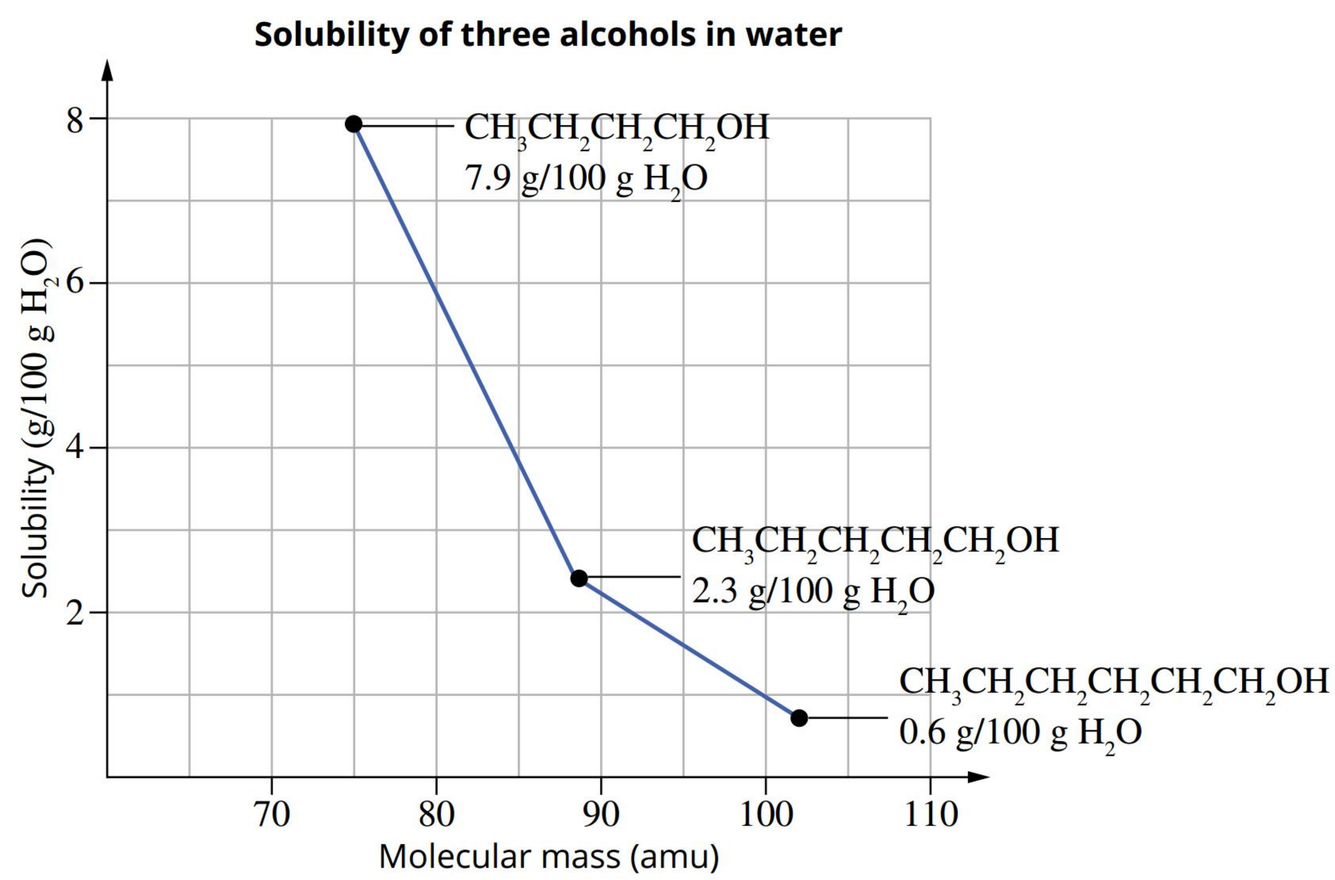


FIGURE 8.7.8 The solubility of alcohols in water decreases with increasing chain length. This trend is also observed for other polar organic compounds such as carboxylic acids.

Like the alcohols, the solubility of the carboxylic acids decreases as the acids increase in size. While the first four members of the carboxylic acid homologous series are highly soluble in water, only the first two members of the alcohol series are highly soluble. This relates to the fact that carboxylic acids ionise in water and can form hydrogen bonds between water molecules with their carbonyl group as well as their hydroxyl group. Being able to form more strong hydrogen bonds benefits the solubility, as does the fact that these are weak acids that partially ionise in water. Table 8.7.1 shows the solubility of the first ten members of the carboxylic acid homologous series.

i Small alcohols and carboxylic acids are highly soluble in water because they can form hydrogen bonds with the water molecules. Carboxylic acids are generally more soluble in water than alcohols because they partially ionise in water and hydrogen bonding can occur on two sites of the carboxylic acid molecules (the C=O and –OH) compared to just the one on alcohol molecules (the –OH).

TABLE 8.7.1 Solubility of carboxylic acids in water

Name	Condensed structural formula	Number of carbon atoms	Solubility (g per 100 g H_2O)
methanoic acid	HCOOH	1	unlimited
ethanoic acid	CH_3COOH	2	unlimited
propanoic acid	CH_3CH_2COOH	3	unlimited
butanoic acid	$CH_3(CH_2)_2COOH$	4	unlimited
pentanoic acid	$CH_3(CH_2)_3COOH$	5	5.0
hexanoic acid	$CH_3(CH_2)_4COOH$	6	1.1
heptanoic acid	$CH_3(CH_2)_5COOH$	7	0.25
octanoic acid	$CH_3(CH_2)_6COOH$	8	0.07
nonanoic acid	$CH_3(CH_2)_7COOH$	9	0.03
decanoic acid	$CH_3(CH_2)_8COOH$	10	0.015

Solubility in organic solvents

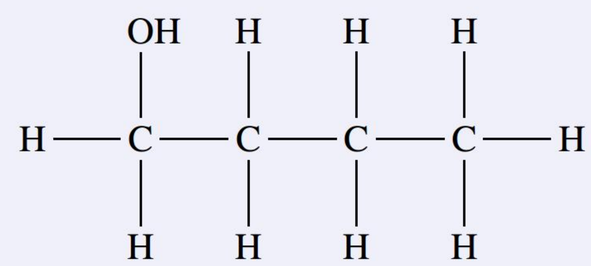
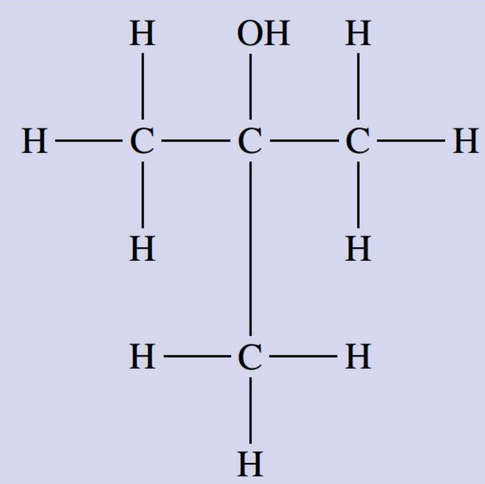
In contrast to their solubility in water, both carboxylic acids and alcohols become more soluble in organic solvents as they get larger. This is because organic solvents, such as hexane, benzene and toluene, are non-polar. Only relatively non-polar alcohols and carboxylic acids with long hydrocarbon chains dissolve well in non-polar solvents.

Small alcohols and carboxylic acids, such as ethanol and ethanoic acid, which are very soluble in water, do not dissolve as well in organic solvents. The dispersion forces between their hydrocarbon chains and the solvent are not strong enough to disrupt the hydrogen bonds that hold the alcohol and carboxylic acid molecules together. Therefore, these organic molecules do not separate and disperse throughout the solvent.

Solubility and molecular shape

The solubility of organic compounds can also be affected by molecular shape. Branched compounds are generally more soluble in water than the corresponding straight-chain compounds. For example, as shown in Table 8.7.2, 2-methylpropan-2-ol is more soluble in water than butan-1-ol. As discussed in Module 8.6, the intermolecular forces that exist between branched molecules are weaker, as the molecules are further apart. In the pure liquid, they do not fit as closely together as straight-chain molecules. Consequently, the intermolecular forces between their molecules are weaker; when the compound is added to water, these weaker forces enable the molecules to separate from each other more easily and mix with the water molecules.

TABLE 8.7.2 A comparison of the solubilities of a straight-chain and branched alcohol

Compound	Molecular formula	Structural formula	Solubility in water at 20°C
butan-1-ol	$C_4H_{10}O$		moderately soluble
2-methylpropan-2-ol	$C_4H_{10}O$		highly soluble

Worked example 8.7.1

CLASSIFYING ORGANIC COMPOUNDS IN TERMS OF THEIR SOLUBILITY IN WATER

Classify the following compounds in order of their increasing solubility in water.

propanoic acid, pentane and butan-2-ol

Thinking	Working
Compare the compounds and identify any relationship between them.	Propanoic acid, pentane and butan-2-ol are members of different homologous series. However, they all have a similar molecular mass, so any difference in their solubility would be due to their different functional groups and how those groups interact with water molecules.
Identify the class of each compound.	Propanoic acid is a carboxylic acid. Pentane is an alkane. Butan-2-ol is an alcohol.
Compare the general solubilities of each class of compound.	Alkanes are non-polar and are therefore insoluble in water. Alcohols can form hydrogen bonds with water; therefore smaller alcohols are very soluble. Carboxylic acids are generally more soluble than other organic compounds because they have two sites on their molecules that can hydrogen bond to water molecules, and they partially ionise in water, further increasing their solubility.
Determine how the solubilities of the listed compounds change and order them in terms of increasing solubility.	Propanoic acid would be more soluble than butan-2-ol in water. Pentane would not be soluble at all. The order, in terms of increasing solubility in water, is therefore: pentane (not soluble) < butan-2-ol < propanoic acid.

➤ Try yourself 8.7.1

CLASSIFYING ORGANIC COMPOUNDS IN TERMS OF THEIR SOLUBILITY IN WATER

Classify the following compounds in order of their increasing solubility in water.
ethanol, butan-1-ol and hexan-1-ol

8.7 Review

SUMMARY

- The non-polar nature of alkanes and alkenes makes them insoluble in water. The relatively weak dispersion forces that they form with the water molecules are not strong enough to compensate for the energy required to break the hydrogen bonds between the water molecules.
- Hydrocarbons readily dissolve in non-polar solvents, such as other hydrocarbons, because they can form similar dispersion forces with the solvent molecules.
- Small alcohols and carboxylic acids dissolve well in water because hydrogen bonds can form between the polar functional groups of the molecules and adjacent water molecules.
- When carboxylic acids dissolve in water, they partially ionise, which produces highly soluble ions. Hydrogen bonding also occurs between both the C=O group and the –OH group on the un-ionised acid molecules and water molecules. Both mechanisms contribute to the increased solubility in water of carboxylic acids when compared to alcohols.
- Alcohols and carboxylic acids become less soluble in water and more soluble in organic solvents as the length of their carbon chain increases. This is because the non-polar hydrocarbon part of their molecules becomes longer, making them less able to form hydrogen bonds with water but more able to form dispersion forces with organic solvents.
- Branched compounds of alcohols and carboxylic acids tend to be more soluble in water than the corresponding straight-chain compounds. This is because, in the pure liquid, branched compounds contain weaker intermolecular forces that can be more easily overcome when the compound is mixed with water.

KEY QUESTIONS

Describe

1 Recall the two factors that affect the solubility of organic compounds.

2 Copy and complete the following paragraph about the solubility of organic compounds. Choose from the following words: (can be used more than once, not all terms are used) **carboxyl, dispersion forces, functional groups, hydrogen bonds, hydroxyl, insoluble, ionise completely, less, more, non-polar, partially ionise, polar, soluble**

Hydrocarbons are _____, which makes them _____ in water, which is _____. The _____ _____ they form with water molecules are not strong enough to overcome the _____ _____ between water molecules. Molecules with _____ _____ that can form hydrogen bonds, such as _____ and _____ groups, more readily dissolve in water. When carboxylic acids dissolve in water, they _____ _____, which makes them _____ soluble than alcohols of a similar size. Non-polar compounds readily dissolve in _____ solvents.

Apply

3 Explain why hydrocarbons are insoluble in water but soluble in non-polar solvents, such as other hydrocarbons.

4 **a** Write an equation showing the partial ionisation of propanoic acid in water.

b Explain how this reaction increases the solubility of propanoic acid in water.

Continued over page

8.7 Review *continued*

Analyse

5 Predict whether each of the following pairs of compounds would be miscible or immiscible.

a pentane and pent-1-ene

b hex-2-ene and water

c octanoic acid and decanoic acid

6 Propan-1-ol, ethanoic acid and butane have a similar molecular mass. Categorise the three compounds in order of:

a increasing solubility in water

b increasing solubility in hexane.

7 Analyse the compounds ethanol and pentan-1-ol and explain why ethanol is more soluble in water than pentan-1-ol, but pentan-1-ol is more soluble in hexane than ethanol.

8 Predict which compound you would expect to be more soluble in water: butan-1-ol or butanoic acid. Explain your answer.

9 The solubilities in water of three carboxylic acids are given in the table below.

Carboxylic acid	Condensed structural formula	Solubility in water at room temperature (mg/mL)
propanoic acid	CH_3CH_2COOH	1000
butanoic acid	$CH_3CH_2CH_2COOH$	60
pentanoic acid	$CH_3(CH_2)_3COOH$	24

a Compare the solubilities of propanoic acid and pentanoic acid in the table above and deduce an explanation for the observed difference.

b Predict how the solubility of 3-methylbutanoic acid would compare with pentanoic acid.

GO TO ➤ **Practical Investigation 4**

Chapter review

08

KEY TERMS

achiral
alcohol
aldehyde
alkane
alkene
alkyl group
alkyl side chain
alkyne
amide
amide functional group
amine
amino functional group
boiling point
carbonyl functional group
carboxyl functional group
carboxylic acid
cis-isomer
cis-trans isomers
chiral
chiral carbon or chiral centre
condensed structural formula
crude oil
dimer
dipole–dipole force
dispersion force
electronegative
electronic configuration
empirical formula
enantiomer
ester
ester functional group
extended structural formula
functional group
geometric isomer
halo functional group
haloalkane
halogen
homologous series
hydrocarbon
hydrocarbon skeleton
hydrogen bond
hydroxyl functional group
immiscible
insoluble
International Union of Pure and Applied Chemistry (IUPAC)
isomer
IUPAC nomenclature
ketone
locan
melting point
miscible
molecular formula
non-polar
optical isomer
organic chemistry
parent alkane
parent molecule
petroleum
plane of symmetry
polar
positional isomer
primary alcohol
primary amide
primary amine
primary haloalkane
saturated molecule
secondary alcohol
secondary haloalkane
skeletal structure
solubility
solvent
stem name
stereoisomer
structural formula
structural isomer
temporary dipole
tertiary alcohol
tertiary haloalkane
tetrahedral
trans-isomer
unsaturated molecule
valence electron
valence number
valence shell electron pair repulsion (VSEPR) theory
vapour
vapour pressure
volatility

KEY QUESTIONS

Describe

1 Determine which molecular formula could represent an alkane.

A C_3H_6
B C_5H_8
C C_6H_6
D C_7H_{16}

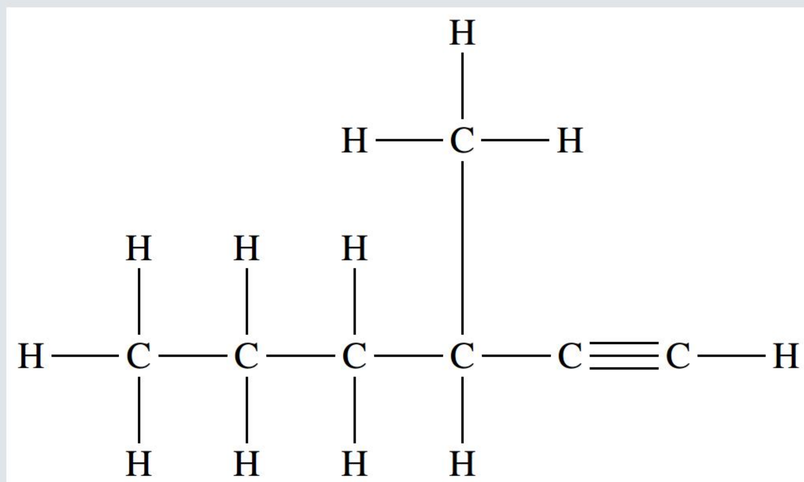
2 Identify which statement about isomers is incorrect.

A Isomers can have very different chemical and physical properties.
B There are two main types of isomers: structural isomers and stereoisomers.
C Isomers can have different molecular formulas as long as they contain the same type of atoms.
D Isomers are molecules that have the same molecular formula but a different arrangement of atoms.

3 Identify the functional group present in alcohols.

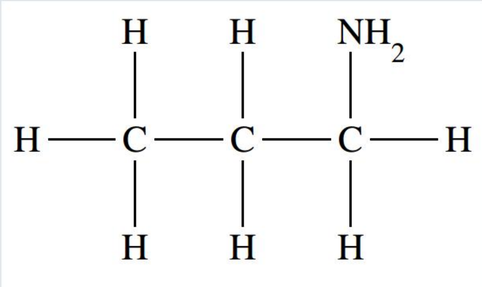
A hydroxyl
B carbonyl
C carboxyl
D alcohol

4 Identify which class of compounds the following molecule belongs to.



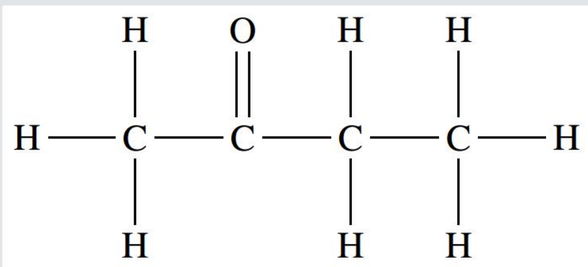
A alkane
B alkene
C alkyne
D an alcohol

5 Identify the class of compound and the functional group present in the following organic molecule.



A class = amine, functional group = amino
B class = ketone, functional group = carbonyl
C class = ester, functional group = ester
D class = amide, functional group = amide

6 Identify the class of compound and the functional group present in the following organic molecule.



A class = ketone, functional group = carbonyl
B class = alcohol, functional group = hydroxyl
C class = aldehyde, functional group = carbonyl
D class = carboxylic acid, functional group = carboxyl

7 Identify what the 'pent' part of the name 2-methylpent-2-ene refers to.
A The molecule is an alkene.
B The double bond is on carbon number 5.
C The molecule contains an alkyl side chain.
D The parent molecule contains five carbon atoms.

8 Identify which statement about boiling points of organic compounds is false.
A Molecular shape affects the boiling points of organic compounds.
B Organic compounds that contain weak intermolecular forces have high boiling points.
C The boiling points of alkanes generally increase as the length of the carbon chain increases.
D The boiling points of organic compounds are dependent on the functional groups present in the compounds.

9 Identify which one of the following statements is true.
A A volatile compound contains weak intermolecular forces of attraction and evaporates easily.
B A volatile compound contains strong intermolecular forces of attraction and evaporates easily.
C A volatile compound contains weak intermolecular forces of attraction and does not evaporate easily.
D A volatile compound contains strong intermolecular forces of attraction and does not evaporate easily.

10 Identify which one of the following statements about the solubility of organic compounds is false.
A Hydrocarbons dissolve well in water.
B Small alcohols and carboxylic acids dissolve well in water.
C A solute will dissolve in a solvent that has similar intermolecular forces.
D Organic compounds that are insoluble in water often dissolve well in organic solvents.

11 Which of the following organic compounds contains a chiral centre?
A 2-bromobutane
B 2,3-dimethylpentane
C 2-methylpropane
D but-1-ene

12 Define the following terms.
a structural isomers
b stereoisomers

13 The IUPAC name of an organic compound usually indicates which functional group is present in the molecule by adding a suffix to the end of the name. For each of the following classes of compounds, state the suffix that would be used.
a alcohol
b ketone
c carboxylic acid

14 State how the boiling points of compounds within a homologous series change as the length of the carbon chain increases.

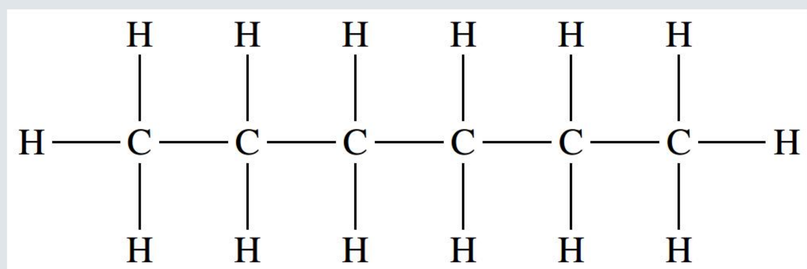
Apply

15 Represent the alkane heptane using its condensed molecular formula.

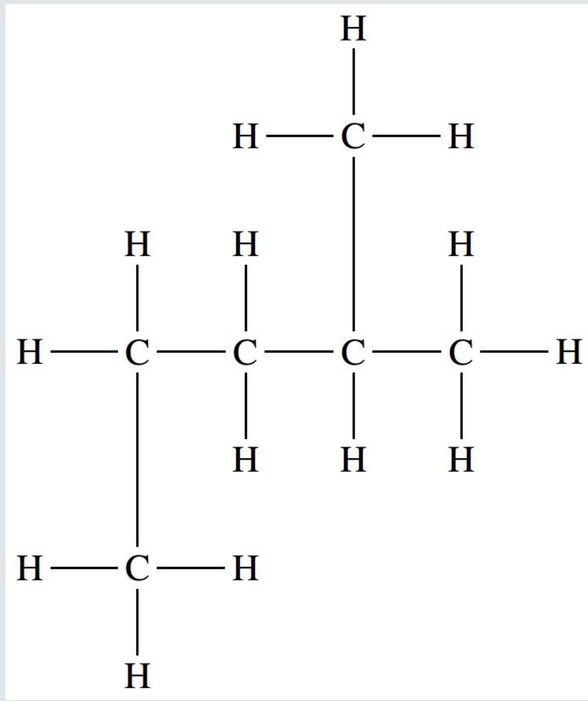
16 The condensed structural formula of 2-methylbutane is $CH_3CH(CH_3)CH_2CH_3$. Draw its corresponding extended structural formula.

17 The structural formulas of three hydrocarbons are shown below. Represent them with their systematic names.

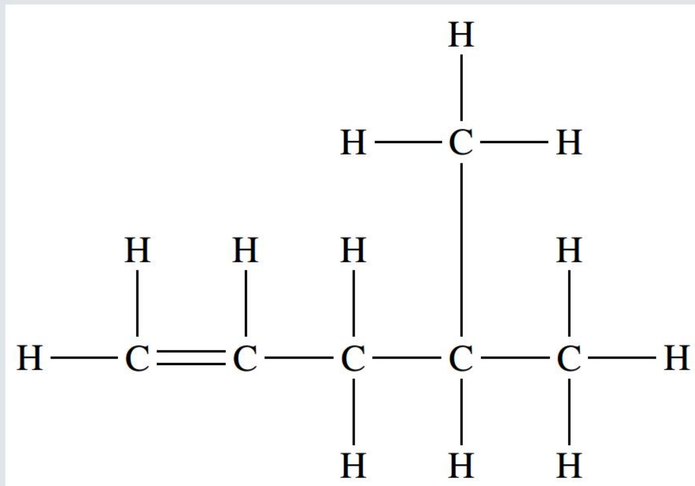
a



b



c



18 The following relates to the hydrocarbon with the molecular formula C_3H_4.

- **a** Identify the class of compounds to which the hydrocarbon belongs.
- **b** Draw the extended structural formula of this hydrocarbon.
- **c** Determine the systematic IUPAC name for the hydrocarbon represented by this structural formula.

19 Determine the structural formula for the following:

- **a** *trans*-1,2-dichloroethene
- **b** *cis*-1,2-dichloroethene

20 Draw the *cis*- and *trans*-isomers of hex-3-ene.

21 Name and describe the position of any functional groups present in the following classes of organic molecules. Provide the condensed structural formula for the class of compound.

- **a** aldehyde
- **b** carboxylic acid

22 Draw an extended structural formula for an ester with four carbon atoms and circle the ester functional group. (Hint: there is more than one possible answer.)

23 Describe the features of the following IUPAC names and explain what information they provide.

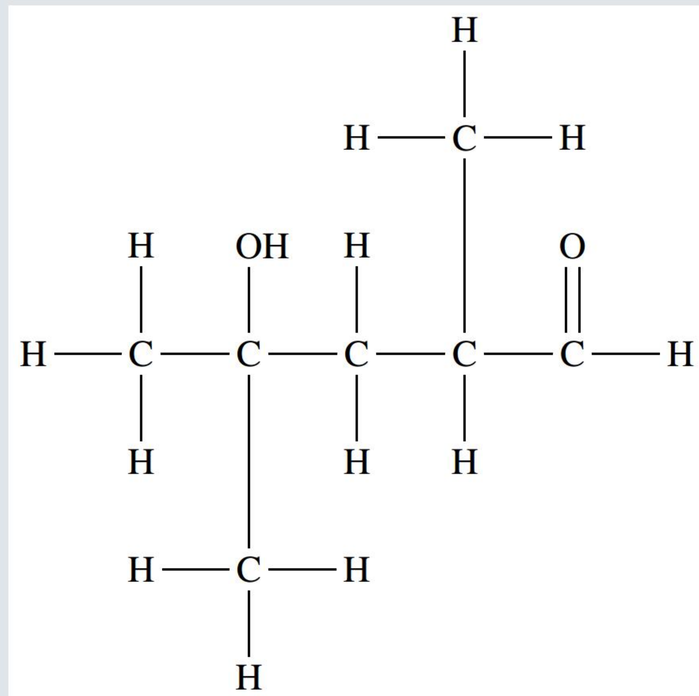
- **a** octan-4-ol
- **b** 2-methylhexan-3-one

Analyse

24 Compare the boiling points of octane and ethane and explain why octane has a higher boiling point than ethane.

25 Compare the solubility of carboxylic acids and alkanes in water and explain why carboxylic acids are more soluble than alkanes.

26 Determine the condensed structural formula and the molecular formula for the following organic molecule by analysing its extended structural formula.



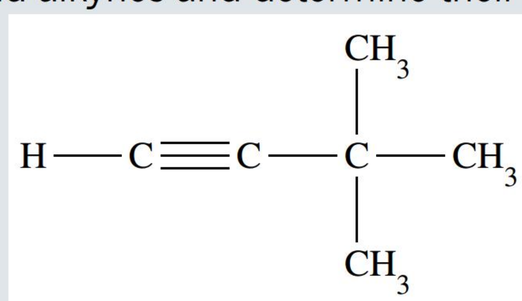
27 Determine the extended structural formula for the following organic compound by analysing its condensed structural formula.
$CH_3CH(CH_3)CO(CH_2)_3NH_2$

28 Analyse the systematic names of the following alkanes and draw their extended structural formulas and corresponding condensed structural formulas.

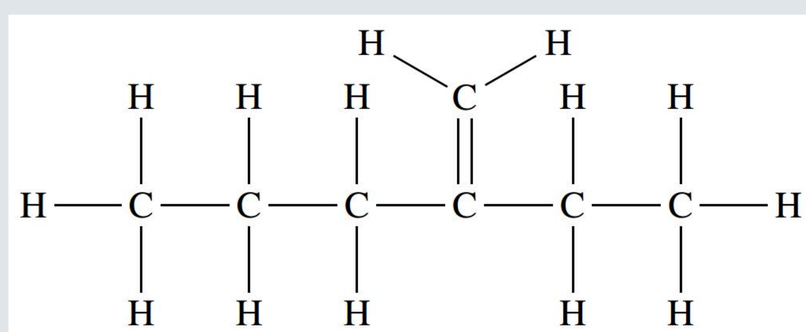
- **a** 2,2,3-trimethylpentane
- **b** 4-ethyl-2-methylhexane

29 Analyse the structural formulas of the following alkenes and alkynes and determine their systematic names.

a



b



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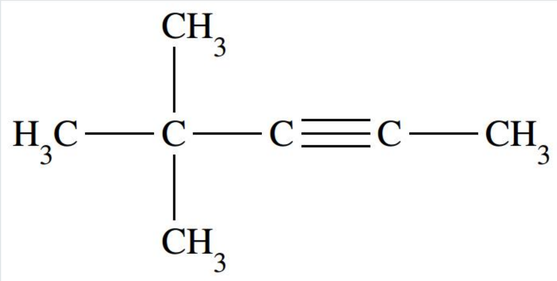


30 Analyse the systematic names of the following hydrocarbons and draw their extended structural formulas.

a 2,3-dimethylpent-2-ene
b 5,5-dimethylhex-2-ene
c 3-ethylhex-3-ene

31 Explore and discuss the following statements.

a The hydrocarbon 2-methylbut-2-yne does not exist.
b The hydrocarbon 2,2-dimethylbut-1-ene does not exist.

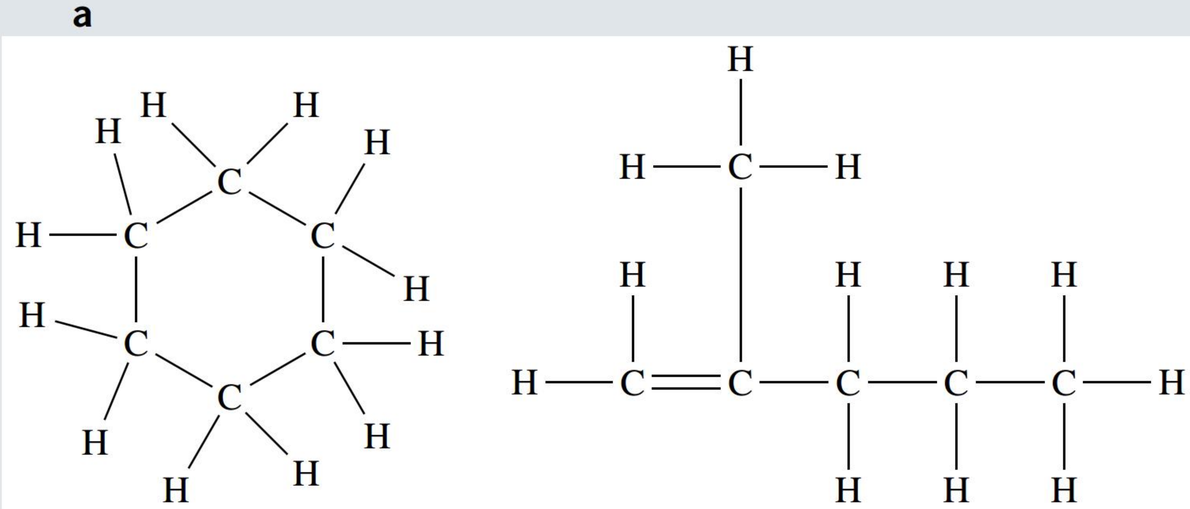
32 Analyse the following incorrect names for three unsaturated hydrocarbons. For each, discuss what is wrong with the name and determine the correct name.

a 2,2-dimethylpent-5-ene
b 1-methylbut-2-ene
c 3-methylbut-2-ene

33 Determine all of the possible structural isomers of alcohols with the molecular formula $C_4H_{10}O$. Determine the systematic IUPAC name for each isomer. Draw structural formulas for each isomer.

34 For each of the following pairs of compounds, determine whether the molecules are structural isomers, identical or unrelated.

a



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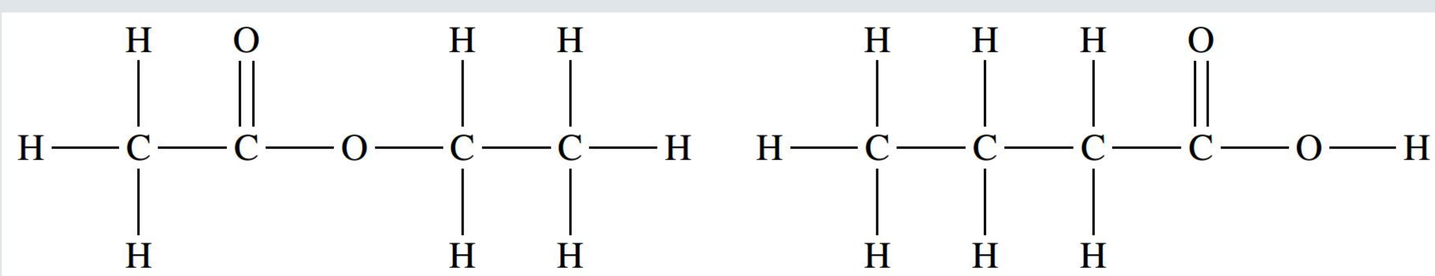
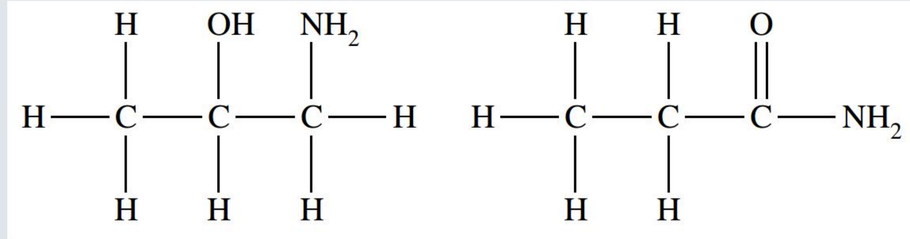


c

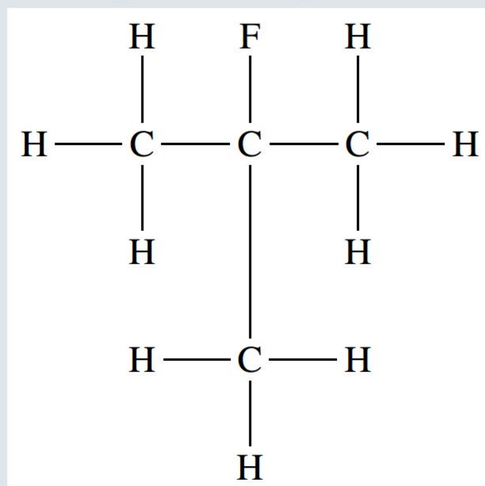


35 Determine in which of the following alkenes *cis-trans* isomers would be possible. Draw and name the *cis-trans* isomers.

a $H_2C{=}CHCH_2CH_3$
b $H_3CHC{=}CHCH_3$
c $H_3CHC{=}CHCl$
d $(H_3C)_2C{=}C(CH_3)_2$

36 Classify the following haloalkanes as primary, secondary or tertiary.

a



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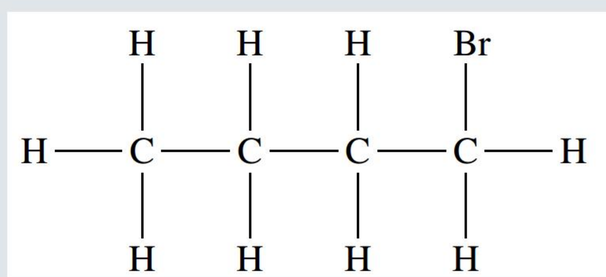

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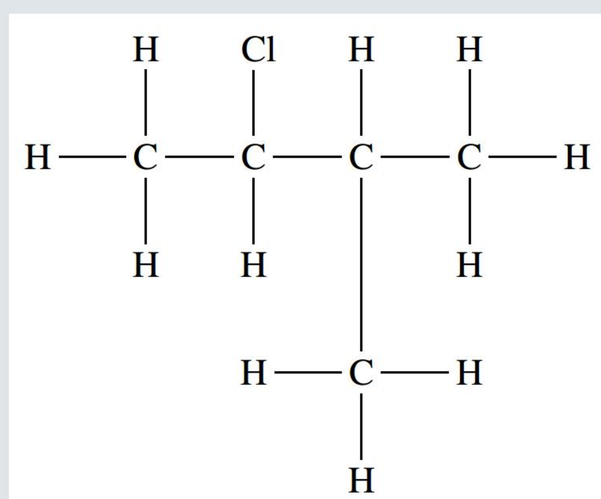


37 Determine the structural formulas for the aldehyde and ketone that have a molecular formula of C_3H_6O.

38 Determine the names of the following compounds from their condensed structural formulas.

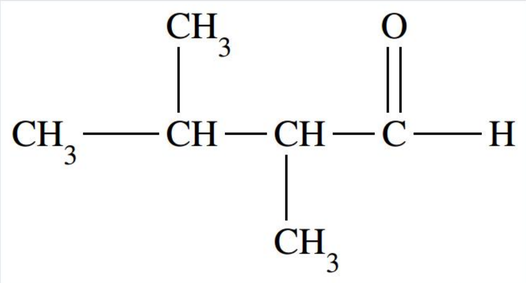
a $CH_3CHOH(CH_2)_3CH_3$

b $CH_3CH_2CH(CH_3)COOH$

c $CH_3COCH(CH_3)CH_2CH_3$

39 Determine the names of the following compounds from their extended structural formulas.

a



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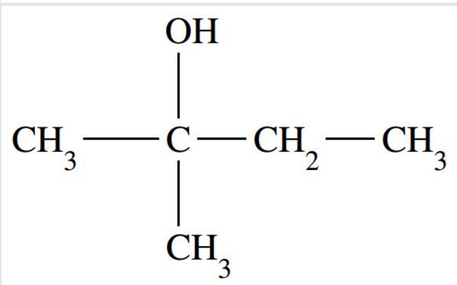

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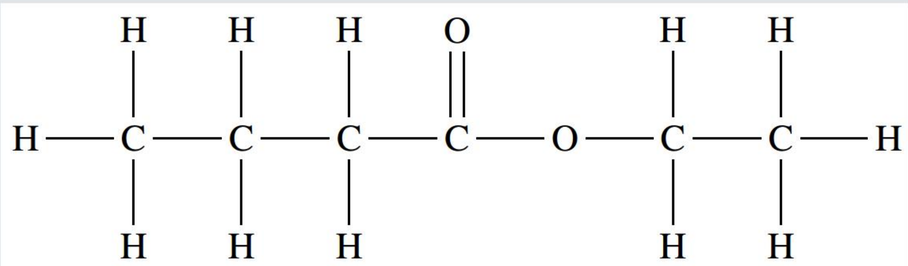


40 From the systematic name 4-ethyl-2-methylhexan-3-one, determine the:

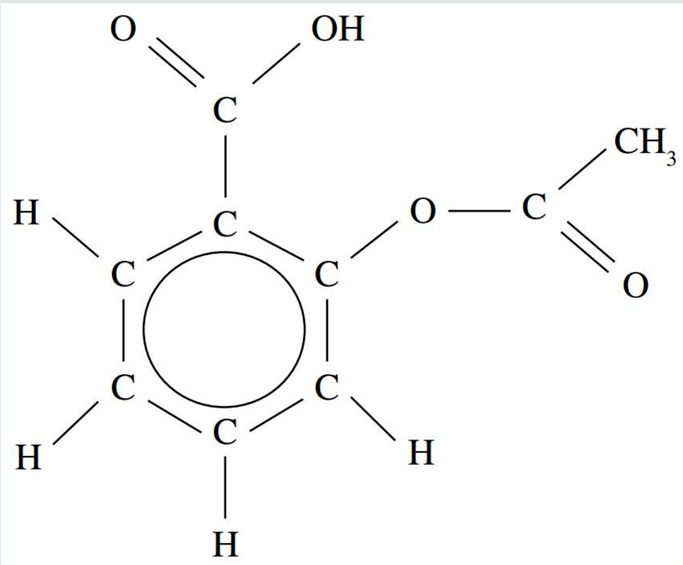
a structural formula

b molecular formula

c empirical formula

d condensed structural formula.

41 The image below shows the structure of aspirin (acetylsalicylic acid).



a Determine the molecular formula for aspirin.

b Determine the empirical formula for aspirin.

c Identify the ester functional group in the structure of aspirin.

d Determine the structure of the alcohol and carboxylic acid that reacted together to produce aspirin.

42 Analyse the following information and draw an isomer that corresponds to the specification in each part of the question.

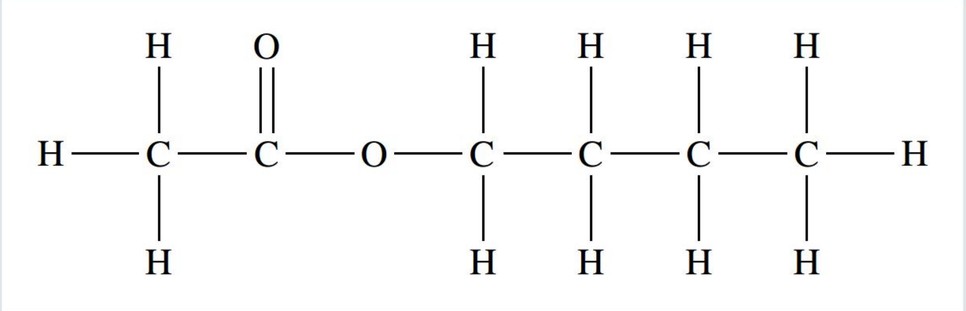
a An aldehyde that is a structural isomer of pentan-2-one.

b A secondary alcohol that is a structural isomer of butan-1-ol.

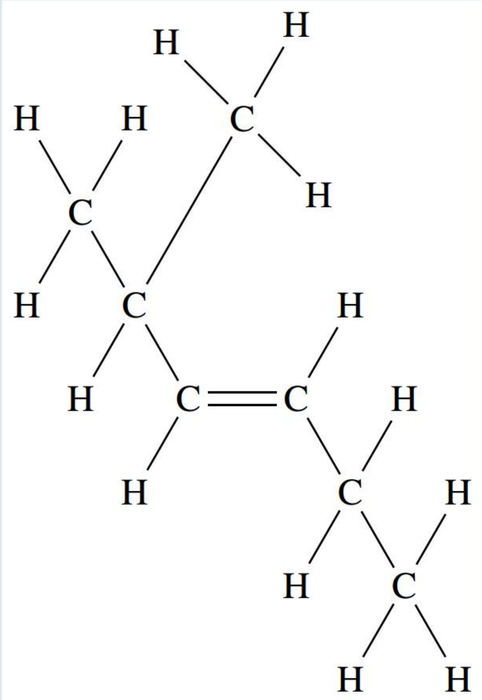
c An alkene that is a structural isomer of but-1-ene.

43 Determine the names of each of the following organic compounds.

a



b



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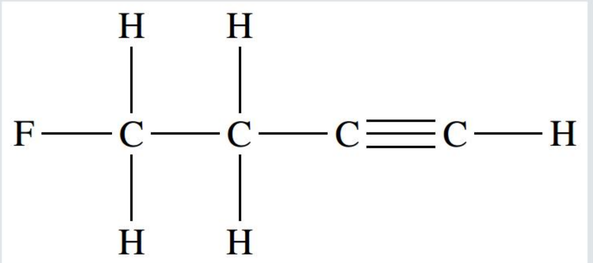

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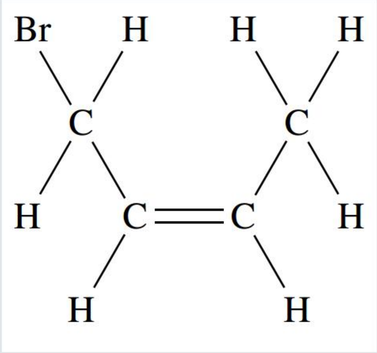


44 Explain how and why the amount of branching present in a compound affects its boiling point. Provide an example to illustrate your explanation.

45 Classify the following compounds in order of increasing boiling point.

a $CH_3CH(CH_3)CH(CH_3)CH_2CH_2OH$
b $CH_3(CH_2)_5CH_2OH$
c $CH_3CH(CH_3)CH_2CH_2CH_2CH_2OH$

46 Analyse the compounds $CH_3CH_2CH_3$, CH_3CH_2OH and HCOOH. Determine which compound:

a has the highest boiling point
b is the most volatile
c has the highest vapour pressure.

47 Explain why, when comparing the effect of functional groups on the boiling points of different homologous series, it is important to compare molecules with a similar molecular mass.

48 The boiling points for some of the members of the homologous series of alkanes are given in the table below.

Alkane	Molecular formula	Boiling point (°C)
methane	CH_4	–162
ethane	C_2H_6	–89
propane	C_3H_8	
butane		–0.5
pentane		
hexane		
heptane		
octane		125
nonane		
decane		174

a Complete the 'Molecular formula' column of the table.
b Plot a graph of boiling point against the number of carbon atoms.
c Draw a line of best fit through the points.
d Alkane X (a straight-chain alkane) boils at 98°C. State the likely identity of this alkane.
e Alkane Y (also a straight-chain alkane) boils at –42°C. State the likely identity of this alkane.
f Use your graph to predict the boiling point of 2-methylbutane.

49 Determine whether each of the following pairs of compounds would be either miscible or immiscible with each other.

a pentane and pent-1-ene
b pent-1-ene and water
c butan-3-ol and pentanoic acid

50 Analyse the compounds CH_3OH, $CH_3(CH_2)_3OH$ and $CH_3(CH_2)_6OH$.

a Classify the compounds in order of increasing solubility in water.
b Explain your answer to part **a**.
c Classify the compounds in order of increasing solubility in hexane.
d Explain your answer to part **c**.

Interpret

51 An organic chemist concludes that an unknown haloalkane with a molecular formula of $C_5H_{11}Cl$ contains a tertiary chlorine atom. Determine a possible structure and name for this organic compound.

52 Determine the three structural isomers that fall into the organic classes of esters or carboxylic acids for the organic compounds with molecular formula $C_3H_6O_2$. Draw and name them. Analyse their structures and discuss how their boiling points would differ.

53 An unknown organic compound was analysed in the laboratory and was found to be highly soluble in water and to have a boiling point of 163°C. It was found that the compound had a molar mass of 88.1 g mol^{-1}, was made up of carbon, hydrogen and oxygen, and contained a carbonyl group. Assess the information given and determine a possible structure and name for this organic compound.

54 The strength of the intermolecular forces present can greatly affect the boiling point of an organic compound.

a Research and design an experiment that will enable you to create a list of increasing boiling points of organic molecules. Your list should include alkanes, alkenes, alcohols and carboxylic acids.
b Determine the expected order of boiling points for your experiment.
c Explain your proposed order in terms of structure and bonding.

Data analysis

DATA SET 1

The information below applies to Questions 1–5.

TABLE 1 Experimental properties (incomplete) of a range of organic compounds

Name	State at 25°C	Molar mass (g mol^{-1})	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa at 20°C)	Solubility in water (g/100 mL)
2-methylpropan-2-ol	liquid	74.12			4.1	100
2-methylpropane	gas	58.12	–160.0	–11.7		0.00489
4-ethyl-3-methylheptane						
butan-1-ol	liquid	74.12	–89.8	117.6	0.67	6.8
butane	gas	58.12	–138.3	–0.5	na	0.00612
decane	liquid	142.28	–29.7	174.1	0.17	0.00000009
decanoic acid	solid	172.26	31.5	268.7	-	0.015
ethanol	liquid	46.07	–114.1	78.2	5.8	100
methanoic acid	liquid	46.03	8.3	101	4.6	100
octane		114.23	–56.8	126	1.33	0.000066
propyne		40.06	–104	–23.1	-	0.36
propane	gas	44.1	–187.6	–42.1	-	0.007

Question 1 (6 marks)

Determine the condensed structural formula, molecular formula and molar mass for 4-ethyl-3-methylheptane.

a condensed structural formula

b molecular formula

c molar mass

Question 2 (3 marks)

Using the melting and boiling points provided, determine the state of prop-1-yne, octane and decanoic acid at 25°C.

prop-1-yne

octane

decanoic acid

Question 3 (7 marks)

a Draw a graph that compares the melting point to the length of the carbon chain for decane, octane and propane. Add a trend line, if appropriate.

b Describe and explain any apparent trend.

c Use your graph to predict the melting point for butane. Compare this to the value given in the data table.

Question 4 (4 marks)

2-methylpropane is a branched isomer of butane. When a molecule is branched, this tends to weaken any intermolecular forces, as the molecules cannot pack as closely together. Is this statement supported by the data in the table? Explain using two physical properties.

Question 5 (3 marks)

Volatility is not measured directly but can be inferred from the vapour pressure of a liquid. Suggest an explanation for the difference in vapour pressures exhibited by ethanol and butan-1-ol, referring to the structure and bonding of these molecules.

Question 6 (4 marks)
Decane and decanoic acid both have ten carbons in their chain. Describe the differences in boiling point and solubility in water between these two compounds. Refer to their structure and bonding to explain these differences.

Question 7 (4 marks)
Methanoic acid and ethanol have very similar molar masses, yet there is a difference in their volatility. Describe and explain this difference.

CHAPTER 09

Chemical properties and reaction pathways

The versatility of the carbon atom forms the basis for carbon chemistry, also called organic chemistry. It is, however, the functional groups that determine the chemical reactivity of these molecules. These groups increase the chemical reactivity compared to that of alkanes. They are 'value-added extras' that are evident in characteristic chemical properties and functions of carbon-based compounds. In Chapter 8, you learnt about the effect functional groups have on physical properties such as boiling point, solubility and volatility. In this chapter, you will understand more about the chemical reactions of the different classes of organic compounds and how chemists synthesise products by manipulating the conditions and reagents of known reaction pathways.

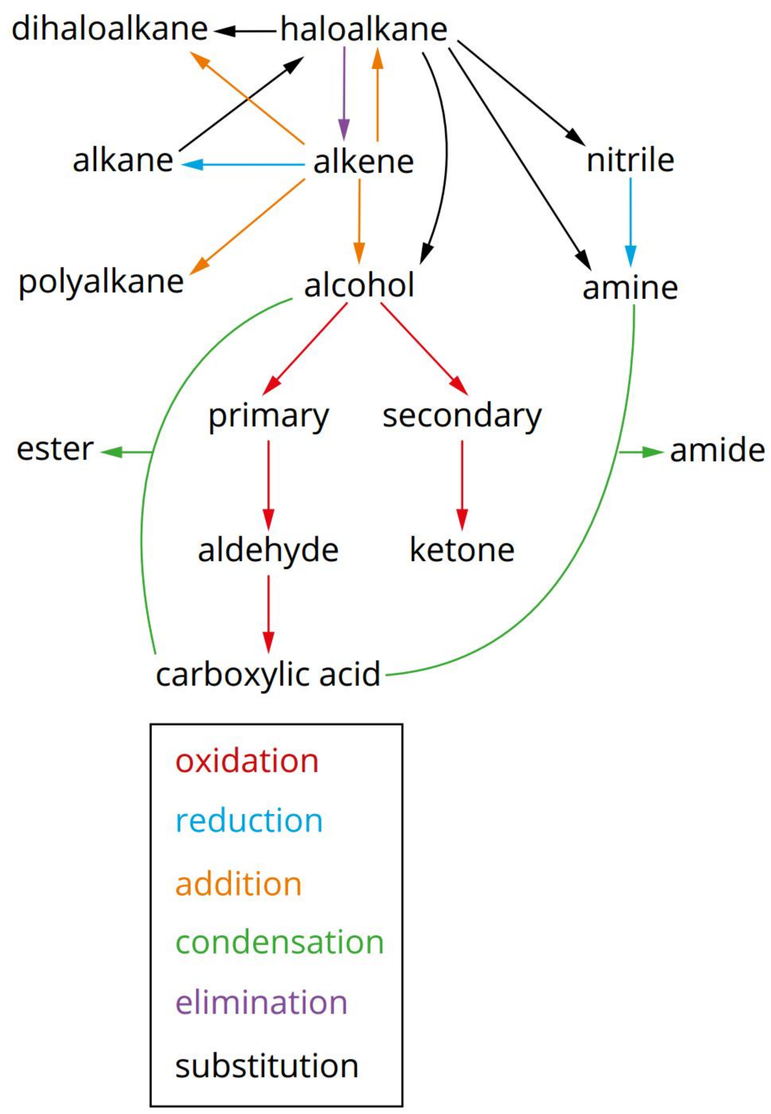
Syllabus subject matter

Topic 1 • Properties and structure of organic materials

ORGANIC REACTIONS AND REACTION PATHWAYS

- Identify that an organic compound displays characteristic chemical properties and undergoes specific reactions based on the functional group present. **9.1**
- Determine, using equations, the reaction of
  - alkanes with halogens (X_2)
  - haloalkanes with halogens (X_2), sodium hydroxide and ammonia
  - alkenes with water, halogens (X_2), hydrogen (H_2) and hydrogen halides (HX)
  - alcohols with hydrogen halides (HX)
  - carboxylic acid with alcohol to form esters, and with amines to form amides. **9.2**, **9.3**
- Determine, using equations, reactions including the
  - oxidation of alcohols
  - combustion of alkanes and alcohols
  - addition of alkenes to form poly(alkenes)
  - reduction of alkynes and alkenes to form alkanes
  - elimination of haloalkanes to form alkenes. **9.2**, **9.3**
- Identify reactions as addition, elimination, substitution or redox (oxidation–reduction). (Reaction mechanisms for substitution and elimination reactions are not required.) **9.2**, **9.3**
- Describe the acid–base properties of carboxylic acids and amines. **9.1**
- Explain that esterification is a reversible reaction. **9.3**
- Discriminate between
  - alkanes and alkenes using bromine water
  - primary, secondary and tertiary alcohols using acidified potassium dichromate (VI) and potassium manganate (VII). **9.1**, **9.3**
- Apply Markovnikov's rule to determine the products for addition reactions of alkenes with hydrogen halides (HX) and water. **9.2**

- Determine reaction pathways, including reagents, condition and chemical equations, given the starting materials and the product/s formed. **9.4**
- Interpret chemical tests to distinguish between alkanes and alkenes; and primary, secondary and tertiary alcohols. **9.1**, **9.3**



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9.1 Understanding the reactivity of organic compounds

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand aspects of functional groups that change the chemical characteristics of a hydrocarbon
- understand key laboratory tests that identify certain classes of organic chemicals.

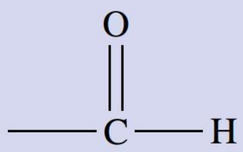
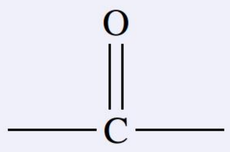
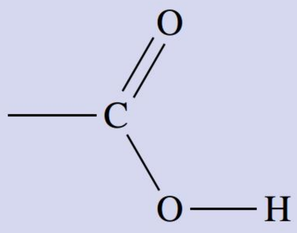
The four valence electrons of the carbon atom are a starting point for building a diverse range of organic compounds. The carbon 'backbone' may contain single, double and triple bonds between carbon atoms, bonded hydrogen atoms, as well as an array of new atoms formed into functional groups (as described in Chapter 8). These functional groups bring features such as high or low electronegativity, charged clouds in the form of non-bonding electrons and areas that are protected by high bond stability. Therefore, each class of organic compound exhibits common chemical characteristics that are identified through the reactions of their functional groups. It is important to remember that the class is the name of the family of compounds and the functional group is their common and characteristic group of atoms. Some strategies for determining the presence of these groups are outlined in this module.

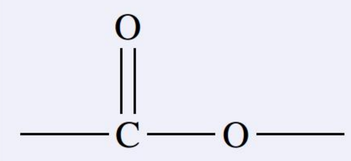
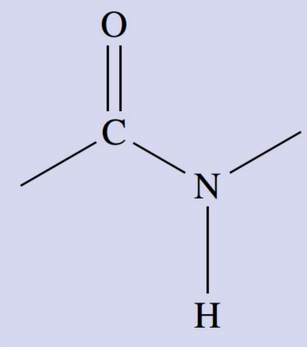
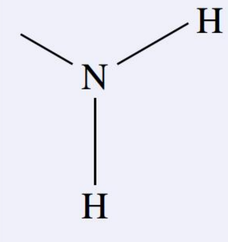
CLASSES OF ORGANIC COMPOUNDS AND THEIR FUNCTIONAL GROUPS

In Chapter 8, you learnt about the many organic compound classes. You can review these by referring to Table 9.1.1. The class is the name of the family of compounds and the functional group is their common and characteristic group of atoms.

> The class is the name of a group or family of similar molecules, and the functional group is their common and characteristic group of atoms.

TABLE 9.1.1 Key classes of organic compounds

Class	Functional group name	Functional group	General formula
alkane	single bond	C–C	R
alkene	double bond	C=C	R=R′
alkyne	triple bond	C≡C	R≡R′
alcohol	hydroxyl	–O–H	ROH
haloalkane	halogen	–X (X = F, Cl, Br, I)	RX
aldehyde	carbonyl		RCHO
ketone	carbonyl		RCOR′
carboxylic acid	carboxyl		RCOOH

ester	ester		RCOOR′
amide	amide		RCONHR
amine			R–NH_2

CHEMICAL PROPERTIES RESULTING FROM FUNCTIONAL GROUPS

Hydrocarbons of the alkane family have a limited range of chemical reactivity. This range increases when functional groups are present. The chemical properties of molecules containing functional groups are diverse because different functional groups allow particular reactions to occur.

Effects of polar bonds

Alkane molecules are non-polar due to the tetrahedral arrangement of bonds around each carbon atom. Also, there is an insignificant difference in electronegativity of atoms (0.4) in a carbon–hydrogen bond. When a functional group containing an atom of higher electronegativity, such as nitrogen, oxygen or a halogen, is attached to a carbon, there is unequal sharing of the electrons in the bond resulting in the formation of a **polar bond**. Carbon has an electronegativity of 2.6, and oxygen has an electronegativity of 3.4. Therefore, the difference in the electronegativity values of C and O (0.8) means that the C–O bond is polar, as shown in Figure 9.1.1. This polarity allows many possible electrostatic charge interactions with other molecules and has myriad consequences for both physical and chemical properties (refer to Chapter 8 for information about physical properties such as boiling point and solubility).

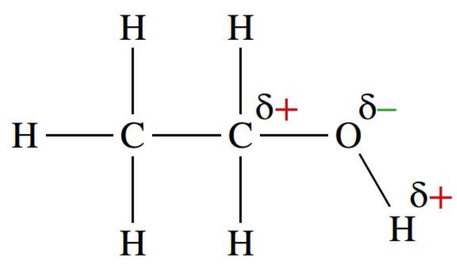


FIGURE 9.1.1 Polar bonds in ethanol

Smaller hydrocarbons exhibit large changes in character; however, larger molecules will still have significant non-polar properties due to the non-polar 'tail', as shown in Figure 9.1.2. A simple way to look at this is with the addition of an OH functional group. When the molecule is small, the polarity of the OH tail is very influential (Figure 9.1.1) but as the chain length of the alcohol increases, the polar influence of the OH functional group lessens (Figure 9.1.2). This means that ethanol is very soluble in water but octanol has low solubility in water ($0.3\,g\,L^{-1}$).

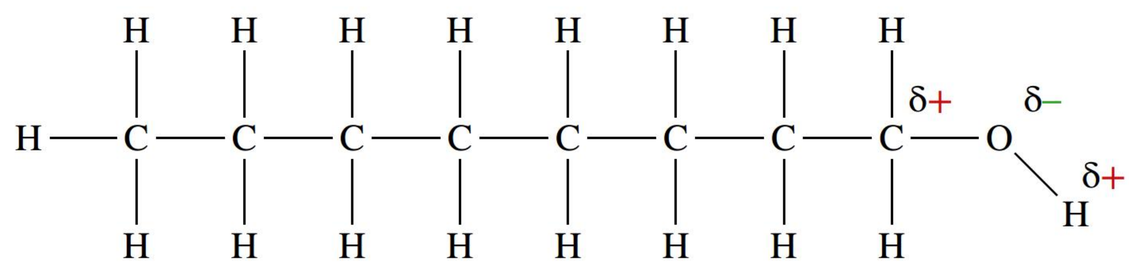


FIGURE 9.1.2 Polar bonds in octanol

Another example of a polar functional group is the carboxyl group (–COOH group) in carboxylic acids. In these molecules, both the C–O single bond and

the C=O double bond are polar. This unequal sharing of electrons weakens the O–H covalent bond in the functional group of the acid. In water, carboxylic acids dissociate, as shown in Figure 9.1.3, as a result of the polarity of the COOH group.

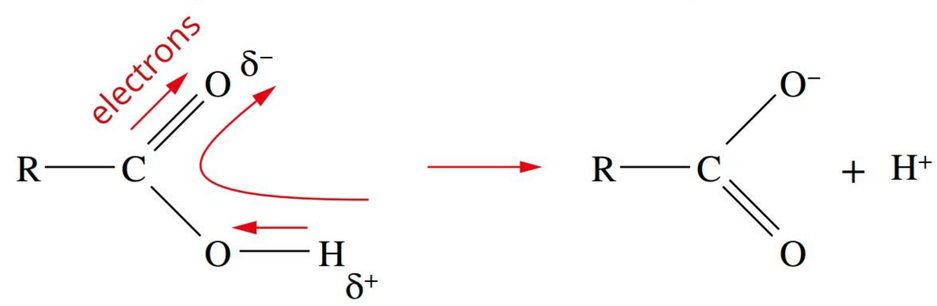


FIGURE 9.1.3 Dissociation of a carboxylic acid

Effects of non-bonding electrons

Carbon atoms in organic molecules always form four covalent bonds. In saturated molecules, these are tetrahedrally arranged single bonds, and they use all carbon's valence electrons. This provides a stable structure free from charge imbalances. Atoms in functional groups often have valence electrons that do not take part in covalent bonding, known as non-bonding electrons. Elements common in functional groups are nitrogen, oxygen and halogens. These atoms have one, two and three pairs of non-bonding electrons, respectively. This means that, in addition to the oxygen atom being more electronegative than carbon, they cause a localised area of partial negative charge in the molecule, as shown in Figure 9.1.4. This creates a dipole in the region of the carbon–oxygen double bond.

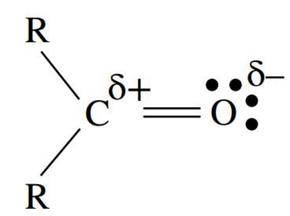


FIGURE 9.1.4 The non-bonding electrons of the carbonyl group in this ketone molecule contribute to the substantial dipole in this ketone.

Species that have a positive charge or an area of partial positive charge are called electrophiles (meaning 'electron-liking'). They react with electron-rich areas. Species that have a negative charge or area of partial negative charge are called nucleophiles (meaning 'nucleus-liking'). Electrostatic charge interactions between these species form the basis for many organic chemistry reactions, in particular the addition of electron-rich groups to the C atom in the carbonyl group. Their strength is often great enough to overcome activation energies associated with reactions. A more detailed study of the mechanism behind these organic reactions is outside the scope of the syllabus.

Effects of double and triple bonds

In alkenes and alkynes, the electrons in the double and triple bonds often take part in chemical reactions. The most common of these are addition reactions; for example, the reaction of an alkene (unsaturated) with hydrogen to form an alkane (saturated). Also, an alkyne is converted to an alkene or alkane. The breaking of double and triple bonds between carbon atoms may require a **catalyst**. These reactions are explained in Module 9.2.

TESTING FOR CLASSES OF ORGANIC COMPOUNDS

Laboratory testing can identify classes of organic compounds. By eliciting reactions involving both the functional group and a coloured compound, different classes of organic compound can be easily distinguished by a colour change. Examples of these tests are shown in Table 9.1.2. Three key examples are determination of organic acids and bases using a pH indicator, determination of an alkene, and determination of primary, secondary and tertiary alcohols.

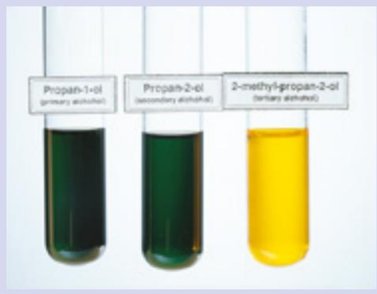
Unsaturated compounds cause a colour change to bromine water.

No change is observed with saturated compounds.

Primary and secondary alcohols cause a colour change to acidified potassium dichromate.

No change is observed with tertiary alcohols.

TABLE 9.1.2 Summary of some tests for classes of organic compounds

Class detected	Test	Result	Chemical process
carboxylic acids	add to water and test for pH		dissociation of the acid and release of H^+ ions into the solution
amines	add to water and test for pH		ionisation of the base and release of OH^- ions into the solution
alkenes	add bromine water; a colour change from brownish-red to colourless indicates an alkene		two bromine atoms are added to the molecule at the position of the double bond; refer to Module 9.2
1°, 2° and 3° alcohols	add acidified potassium dichromate (or potassium permanganate) and heat; a colour change from yellow to green is observed for 1° and 2° but not 3° alcohols		1° alcohols will react to form carboxylic acids, 2° alcohols will react to form ketones and 3° alcohols will not react; refer to Module 9.3

Determination of organic acids and bases using a pH indicator

The strong polarity of the hydroxyl group on the carboxylic acid molecule will result in easy dissociation of the molecule when added to water. This means that H^+ is released into solution, producing H_3O^+ as shown below. The water molecule is a Brønsted–Lowry base. By using a pH indicator, or by adding a carbonate, the presence of acid in solution is detected.

$$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$$

Amines are organic bases that react with water and produce OH^- ions in solution as shown below. The water molecule is a Brønsted–Lowry acid. A pH indicator will reveal a high pH for an amine in solution.

$$CH_3CH_2NH_2 + H_2O \rightarrow CH_3CH_2NH_3^+ + OH^-$$

Determination of an alkene

The presence of a C=C double bond in alkenes compared to saturated alkanes is detected using bromine water. The brownish-red bromine solution will become colourless in the presence of an alkene. Two bromine atoms are added in the position of the double bond, which is converted to a single bond (Figure 9.1.5). This reaction also occurs with alkynes and is described further in Module 9.2. Nowadays the use of bromine in the laboratory is limited due to its hazardous nature. More commonly the presence of a double bond is determined using potassium permanganate, which decolourises from purple in the presence of a double bond.

Potassium permanganate is also known as potassium manganate (VII).

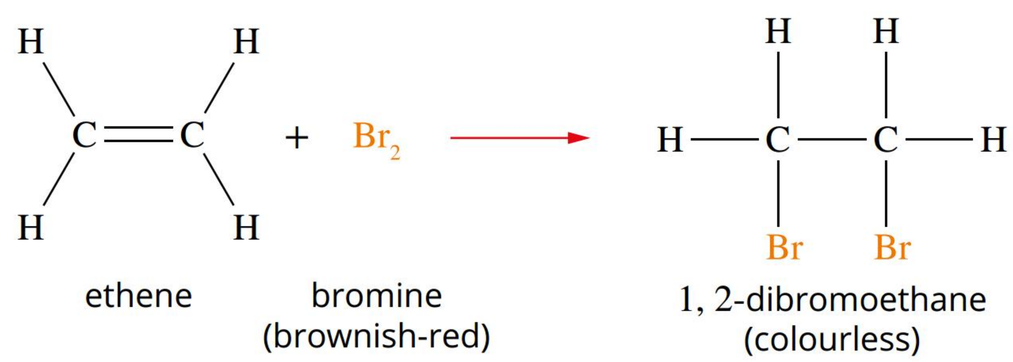


FIGURE 9.1.5 Determination of an alkene using bromine solution

Determination of primary, secondary and tertiary alcohols

You will recall from Module 8.4 that in primary, secondary and tertiary alcohols (commonly represented as 1°, 2° and 3° alcohols, respectively), the hydroxyl group is positioned in different parts of the molecule, as shown in Figure 9.1.6. This results in changes to the molecule's reactivity. By using a strong oxidising agent such as acidified potassium dichromate ($H^+/K_2Cr_2O_7$), or potassium permanganate ($H^+/KMnO_4$), alternate colour changes are observed. 1° alcohols will react to form an aldehyde and then be further oxidised to a carboxylic acid (colour change from yellow to green); 2° alcohols will react to form a ketone but not react further to the carboxylic acid (colour change from yellow to green); and 3° alcohols will not react (solution remains yellow). These oxidation reactions are further explained in Module 9.3.

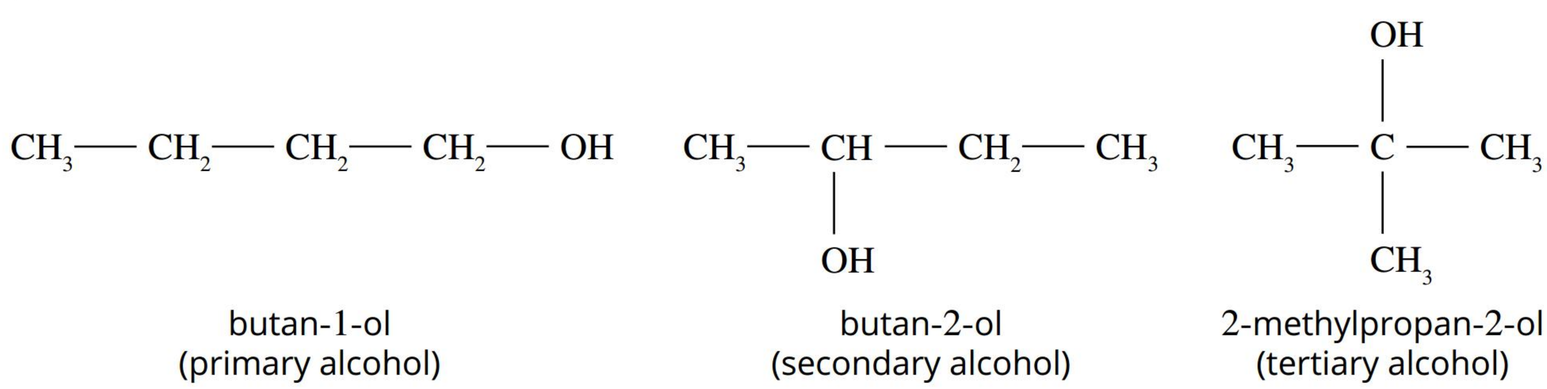


FIGURE 9.1.6 Examples of 1°, 2° and 3° alcohols showing the different positions of the hydroxyl group (–OH)

9.1 Review

SUMMARY

- Organic compounds are grouped into classes. Each class is characterised by a common functional group.
- Reactivity in organic molecules is conferred by the functional groups present and these reactions can be used to identify classes.
- Highly electronegative atoms in functional groups cause bond polarity and areas of partial negative and positive charge.
- A polar bond, non-bonding electrons and electrons in double and triple bonds are areas of charge disparity in molecules that attract oppositely charged species, often leading to a chemical reaction.
- A molecule containing a carboxyl group will exhibit a low pH in water, and a molecule containing an amino group will exhibit a high pH in water. These are Brønsted–Lowry reactions with water.
- A molecule containing a carbon–carbon double or triple bond will turn bromine water from brownish-red to colourless.
- A molecule containing a hydroxyl group as a 1° or 2° alcohol can be oxidised by an oxidising agent, often showing a colour change, whereas a 3° alcohol cannot be oxidised and the oxidising agent will show no colour change.

Continued over page

9.1 Review *continued*

KEY QUESTIONS

Describe

1 Use Table 9.1.1 on page 351 to identify which classes of organic compounds contain:

- **a** oxygen
- **b** nitrogen
- **c** a halogen.

Apply

2 Determine whether ethanoic acid solution or ethanamine would have a higher pH. Provide a reason for your answer.

3 A sample known to contain an alcohol with four carbon atoms does not react (produces no colour change) with acidified potassium dichromate. Draw a possible structure for this alcohol molecule.

4 Two alcohols, propanol and decanol, are placed in separate test tubes containing water and then stirred. Explain why after several minutes the liquids in one test tube separate into two distinct layers but this does not happen in the other test tube.

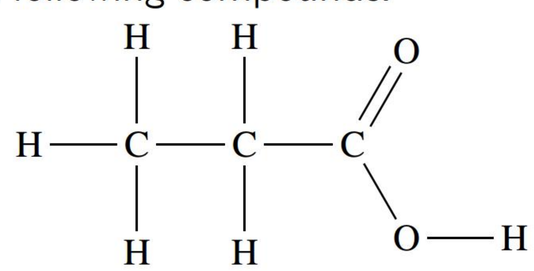
5 2-methylbutan-2-ol, propan-2-ol, hexanol and pentan-3-ol are tested with acidified potassium dichromate. Describe expected colour change(s).

6 Write the chemical equation for $CH_3CH_2CH_2COOH$ acting as a Brønsted-Lowry acid in water.

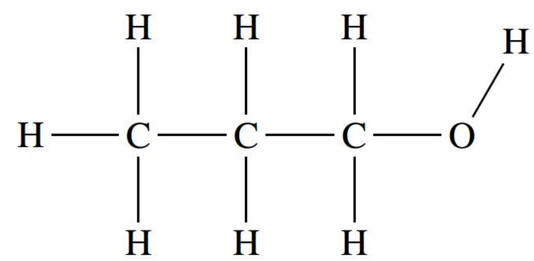
Analyse

7 Determine what test/s you would perform to identify the following compounds.

a



b



8 Two samples of cooking oil containing either a saturated or unsaturated fat were added to test tubes containing bromine water and shaken. After reacting, the oil and water were allowed to reseparate.

Explain how your observations can help you determine which sample is olive oil (unsaturated) and which is coconut oil (saturated).

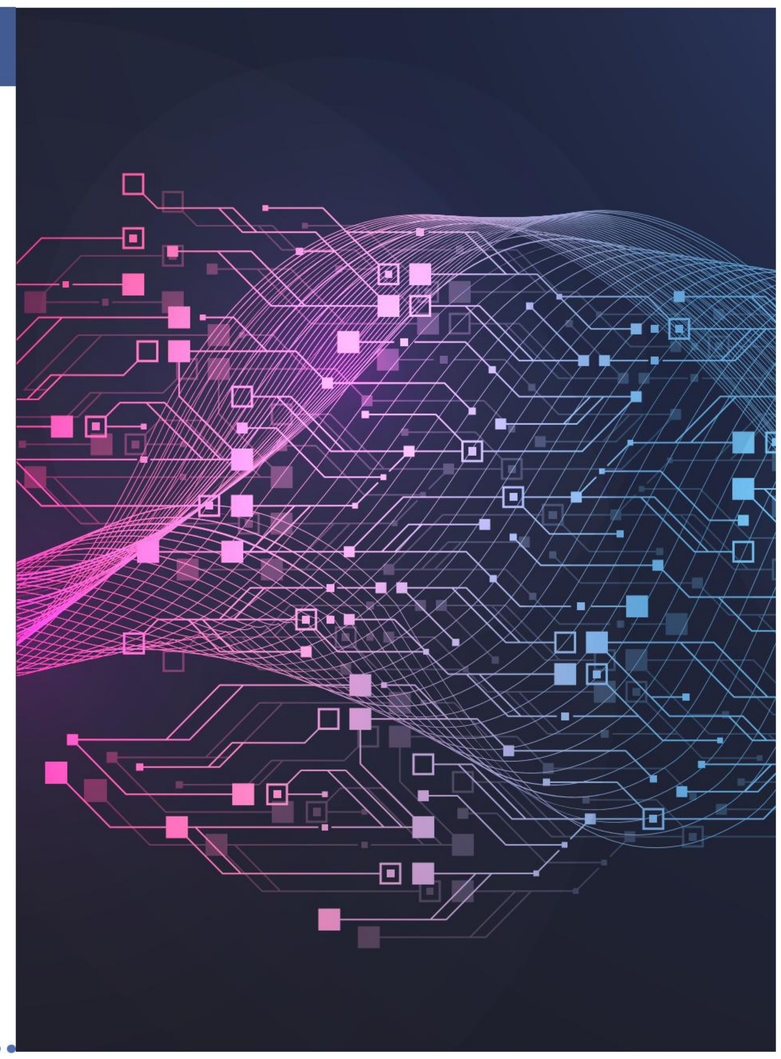
9 Write the chemical equation which describes how $CH_3CH_2NH_2$ dissociates in water and identify the Brønsted-Lowry acid.

10 Identify the conjugate base when propanamine dissociates in water.

9.2 Chemical reactions of alkanes, haloalkanes and alkenes

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that alkanes and alkenes undergo combustion
- understand that alkanes undergo substitution reactions with halogens (Reaction 1)
- understand that haloalkanes undergo substitution reactions with halogens (Reaction 2), ammonia (Reaction 4) and hydroxide ion (Reaction 11)
- understand that alkenes undergo addition reactions with hydrogen (Reaction 5, also known as reduction), halogens (Reaction 6), water (Reaction 7) and hydrogen halides (Reaction 8)
- understand that alkenes undergo addition polymerisation reactions to form polymers (Reaction 10)
- recognise that addition of a hydrogen halide to an alkene (Reaction 8) can be reversed—this is called an elimination reaction (Reaction 9)
- recognise the specific reactions of alkanes and alkenes that require certain conditions to proceed
- explain organic chemistry reactions using chemical equations and structural formulas.



The simpler hydrocarbons such as alkanes, haloalkanes and alkenes undergo chemical change in several key ways. The reactions discussed in this module are **substitution reactions** (reacting atom(s) are exchanged for others in the molecule), **addition reactions** (atom(s) are added to the molecule, this can include reduction), **elimination reactions** (a pair of atoms in the molecule are removed and a double bond formed) and **combustion**. These reactions are driven by forces integral to polar bonds, multiple covalent bonds and non-bonding pairs (described in Module 9.1); however, the mechanism of each reaction is outside the scope of the syllabus and so will not be discussed here. The reactions described in this module are introduced in Figure 9.2.1.

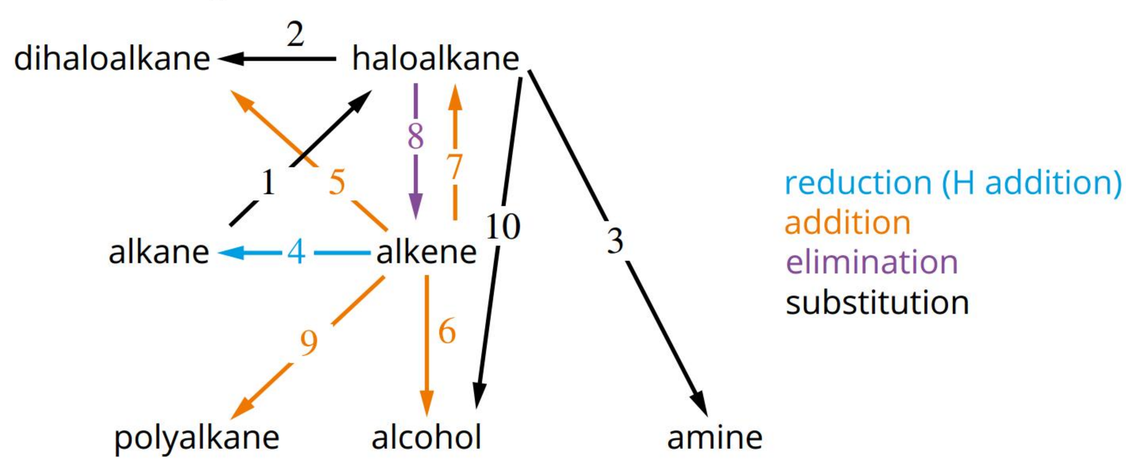


FIGURE 9.2.1 Reactions described in this module, showing the order of description

A summary of the **reaction pathways** described in this module is shown in Figure 9.2.2. This diagram shows chemical structures and reaction conditions for reactions of alkanes, haloalkanes and alkenes.

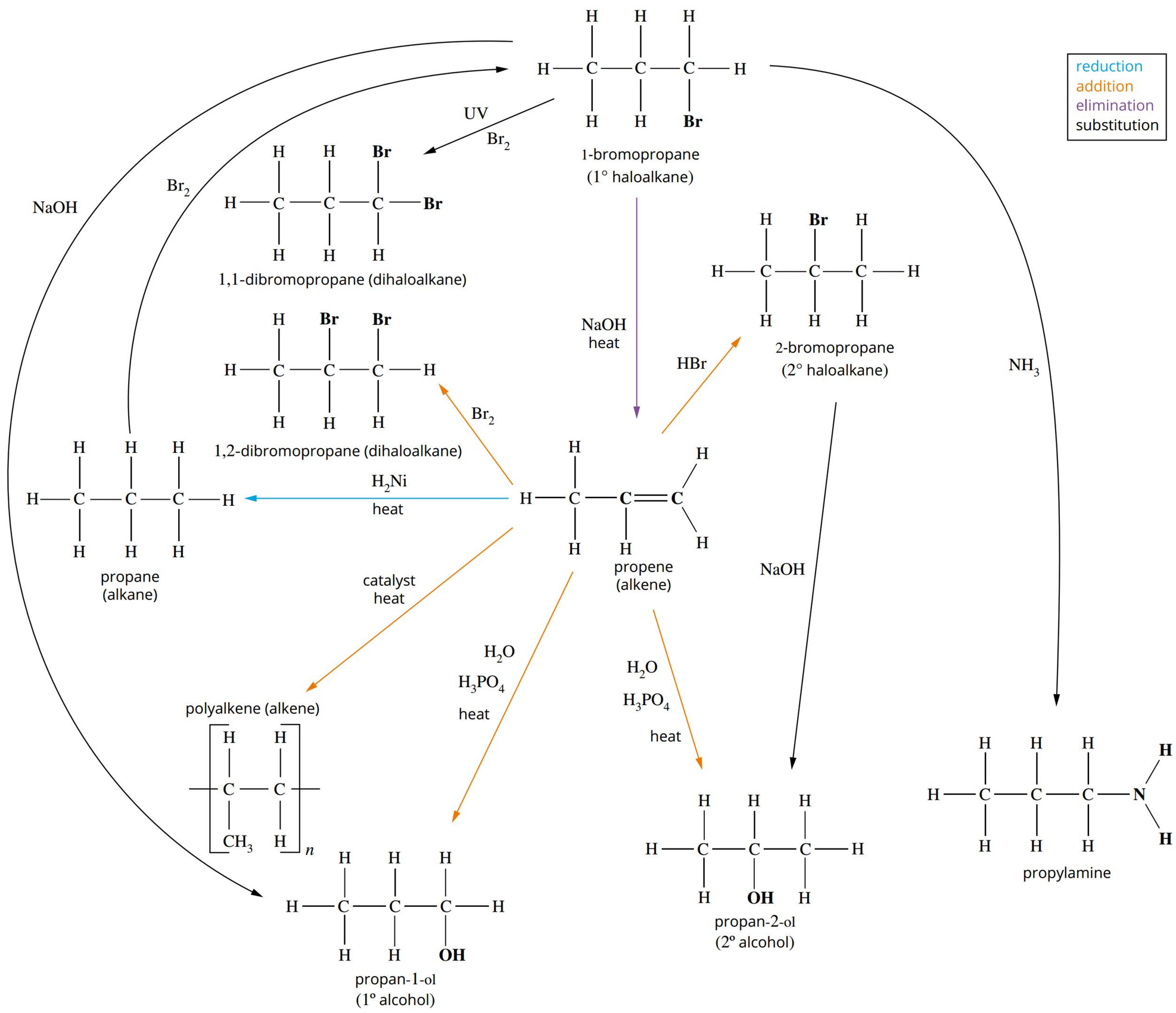


FIGURE 9.2.2 Chemical structures and reaction conditions for reactions of alkanes, haloalkanes and alkenes. Reduction, addition, elimination and substitution reactions are shown. Functional groups are shown in bold.

FIGURE 9.2.3 Methane undergoes complete combustion in a Bunsen burner when the air holes are open.

COMBUSTION OF ALKANES

A reaction of alkanes that has great significance to our society is combustion. As fuels, any member of the alkane class can provide energy. For example, the alkane mixture known as crude oil provides:

- smaller molecules such as methane and propane for use as gas fuels
- octane, nonane and decane as major components of petroleum
- larger molecules ($C_{10}H_{22}$ to $C_{15}H_{32}$) for use as diesel fuels.

Alkanes react with oxygen to produce carbon dioxide and water and significant amounts of energy. It is an exothermic **oxidation–reduction reaction**. If the supply of oxygen is plentiful, the products of combustion will be carbon dioxide and water. This is known as **complete combustion** and is represented by the following balanced reaction:

$$C_xH_y(g) + (x + (y/4))O_2(g) \rightarrow xCO_2(g) + (y/2)H_2O(g) + \text{energy}$$

Combustion and fuels (including incomplete combustion) are explained in Unit 1. Figure 9.2.3 shows natural gas (primarily methane) undergoing complete combustion in a Bunsen burner when the air holes are open. The chemical equation for the complete combustion of methane is:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \text{energy}$$

Octane is a major component of petroleum. The balanced reaction for the complete combustion of octane is:

$$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g) + \text{energy}$$

SUBSTITUTION REACTIONS OF ALKANES

A substitution reaction occurs when an atom or functional group in a molecule is replaced or 'substituted' by another atom or group. Alkanes are saturated hydrocarbons and undergo substitution reactions with halogens, such as chlorine and bromine, to produce haloalkanes. At room temperature and in the dark, a reaction vessel containing a mixture of an alkane such as methane and chlorine gas will not react. For the substitution reaction to occur, the reaction must be initiated by ultraviolet (UV) light.

The reaction between methane and chlorine in the presence of UV light is given by the equation:

$$CH_4(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_3Cl(g) + HCl(g)$$

For each molecule of chlorine gas (Cl_2) that reacts, a hydrogen atom on the alkane is replaced by a chlorine atom.

Chemists write the general equation for an alkane reacting with chlorine in shorthand form as:

$$RH + Cl_2 \xrightarrow{\text{UV light}} RCl + HCl$$

For all general equations, R represents an **alkyl group**.

Chloromethane is the substitution product of this reaction. As the reaction proceeds, the chloromethane product may continue to react with another chlorine molecule. If this occurs, dichloromethane (CH_2Cl_2, a dihaloalkane) is produced.

$$RCl + Cl_2 \rightarrow RCl_2 + HCl$$

If enough chlorine is available, further reactions can result in all four hydrogen atoms of the original methane molecule being substituted by chlorine atoms, as shown in Figure 9.2.4. The different substituted products have different boiling points, so they may be separated from one another by **fractional distillation**.

Substitution reactions of alkanes using excess chlorine gas can result in a mixture of chloroalkane products with varying levels of substitution.

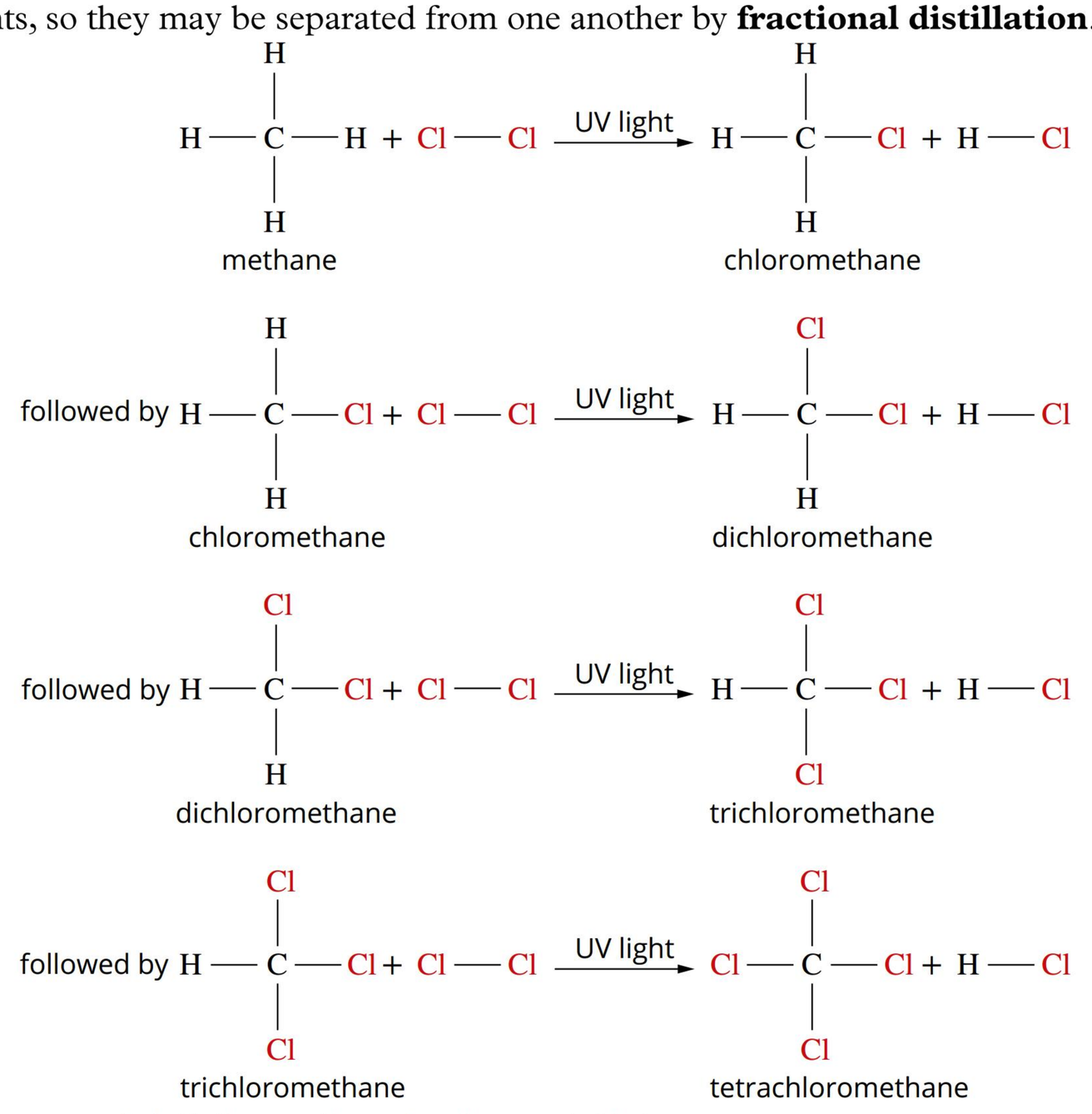


FIGURE 9.2.4 Substitution reactions of methane and chlorine

Substitution reactions of haloalkanes

A substitution reaction occurs when an atom or functional group in a molecule is replaced by another atom or group.

In haloalkanes, the large electronegativity difference between halogen and carbon atoms means that the carbon–halogen bond is polar. This makes the bond weaker than one without a dipole. Species such as another halogen ion, ammonia or hydroxide ion (OH^-) can be substituted for the halogen in the polar bond. The new organic product is a different haloalkane, an amine or an alcohol, respectively. For example, in the reaction shown below, a bromine atom takes the place of the chlorine atom in the haloalkane. Because the chlorine atom of the chloroalkane has been replaced, this is a substitution reaction:

$$KBr + CH_3Cl \rightarrow CH_3Br + KCl$$

Ammonia also reacts with haloalkanes in substitution reactions. The product of these reactions is an amine. The general equation for the formation of an amine by substitution with ammonia is:

$$RCl + NH_3 \rightarrow RNH_2 + HCl$$

Figure 9.2.5 shows the reaction of chloroethane with ammonia. The substitution reaction does not require a catalyst and produces ethanamine as the product. The production of propan-2-amine by reaction of 2-chloropropane with ammonia is also shown. Other haloalkanes containing fluorine, bromine and iodine also undergo substitution reactions with ammonia to produce the corresponding amines.

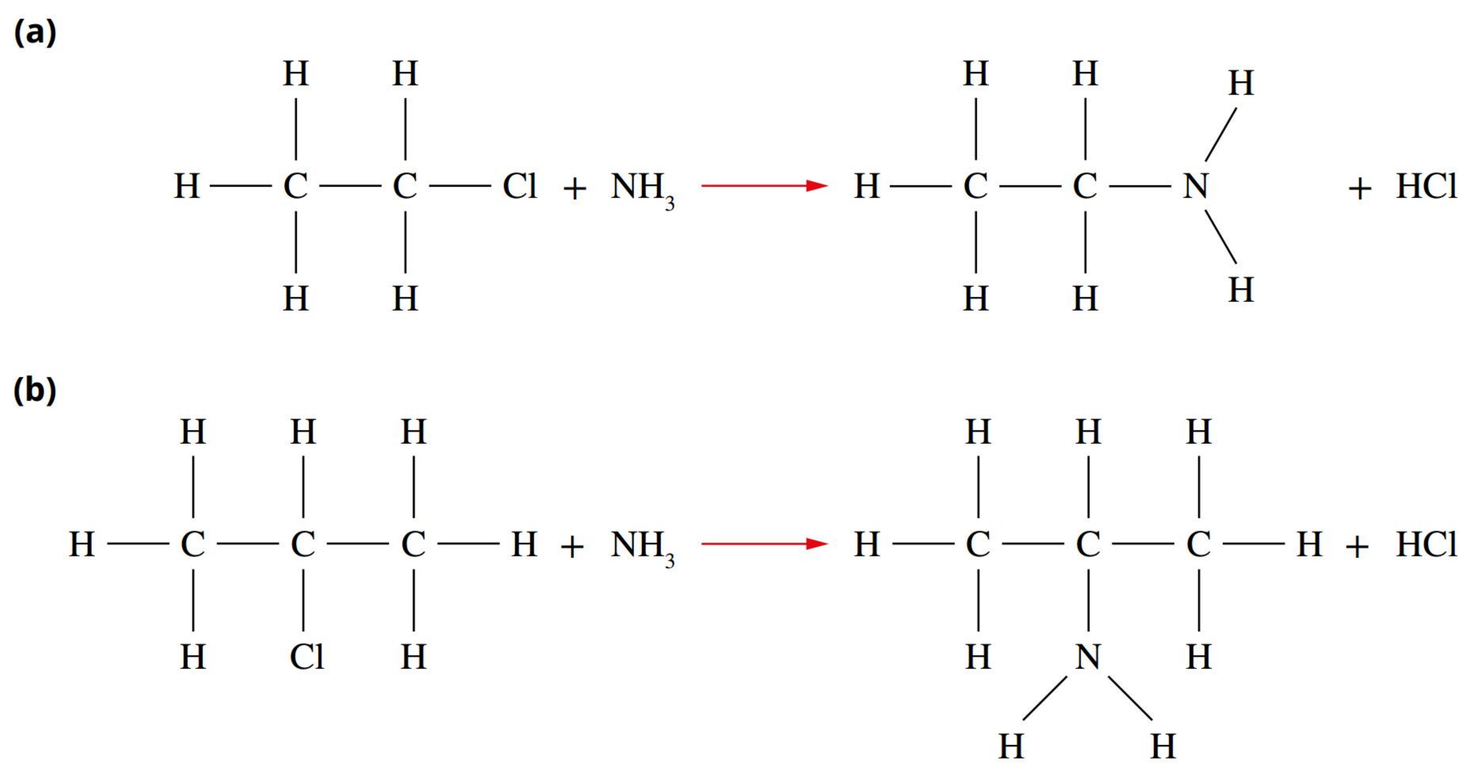


FIGURE 9.2.5 (a) Reaction of chloroethane with ammonia produces ethanamine. (b) Reaction of 2-chloropropane with ammonia produces propan-2-amine.

Sodium hydroxide also reacts with haloalkanes in substitution reactions. The product of these reactions is an alcohol. The general equation for the formation of an alcohol by substitution of a haloalkane with hydroxide is:

$$RCl + NaOH \rightarrow ROH + NaCl$$

In the presence of sodium hydroxide or potassium hydroxide, a haloalkane can undergo the substitution reaction, or when heat is applied, an elimination reaction is favoured. This means that for the same reactants, a haloalkane and sodium hydroxide, changing the conditions of the reaction will alter the products. Lower temperatures favour a substitution reaction (producing an alcohol) and higher temperatures favour elimination reaction (producing an alkene). The elimination reaction is favoured when the reaction is done in ethanol, not water. Tertiary haloalkanes usually undergo elimination and primary haloalkanes usually undergo substitution in the presence of sodium hydroxide solution or potassium hydroxide solution. Table 9.2.1 list the factors that influence substitution or elimination.

TABLE 9.2.1 Factors influencing substitution or elimination

Substitution or elimination	
Type of haloalkane	
primary	mainly substitution
secondary	both substitution and elimination
tertiary	mainly elimination
Solvent	
water	encourages substitution
ethanol	encourages elimination
Temperature	
heat	encourages elimination
Sodium hydroxide or potassium hydroxide concentration	
high	encourages elimination

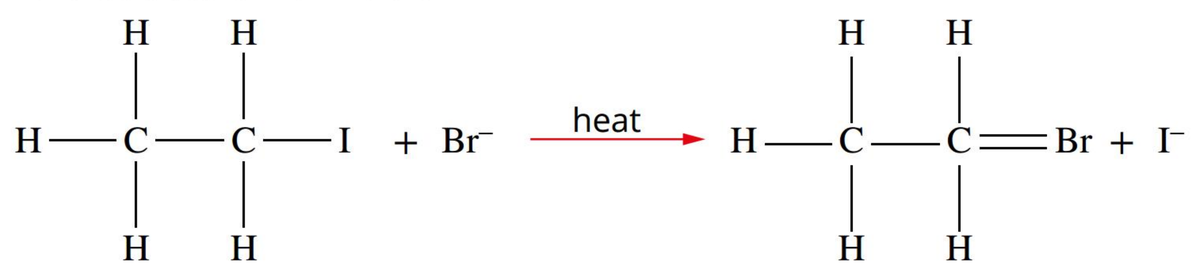
Worked example 9.2.1

DEDUCING A SUBSTITUTION REACTION

Construct the chemical equation and the structural formulas for the substitution reaction between potassium bromide and iodoethane.

Thinking	Working
Identify the reacting organic molecule.	iodoethane (CH_3CH_2I)
Identify the inorganic reactant.	bromide ion Br^-
Recall reactions of haloalkanes and identify the reacting species (refer to Figure 9.2.2 on page 358).	Haloalkanes can undergo substitution reactions with KBr, NH_3, CN^- and OH. So, the reacting species is likely to be Br^- on the inorganic reactant and I on iodoethane.
Substitute the two reacting species.	$CH_3CH_2I + Br^- \xrightarrow{\text{heat}} CH_3CH_2Br + I^-$

Draw the structural formulas.



➤ Try yourself 9.2.1

DEDUCING A SUBSTITUTION REACTION

Construct the chemical equation and the structural formulas for the substitution reaction between ammonia and bromoethane.

A haloalkane can undergo a substitution reaction to form a dihaloalkane, an amine or an alcohol.

ADDITION REACTIONS OF ALKENES

The carbon–carbon double covalent bond in alkenes has a significant effect on the chemical properties of the homologous series. Alkenes are generally more reactive compounds, reacting more readily and with more chemicals than alkanes, which

contain only single bonds. The reactions of alkenes usually involve the addition of a small molecule to the double bond of the alkene. These reactions are called addition reactions.

During addition reactions:

- two reactant molecules combine to form one product molecule
- the C=C double bond becomes a C–C single bond
- an unsaturated compound becomes saturated
- the atoms of the small molecule adding to the alkene are 'added across the double bond', so that one atom or group from the molecule forms a bond to each of the carbon atoms in the double bond
- oxidation states of atoms often change and this evidence indicates that oxidation and reduction (and therefore a redox reaction) is occurring.

A typical addition reaction is shown in Figure 9.2.6. X_2 designates any halogen molecule.

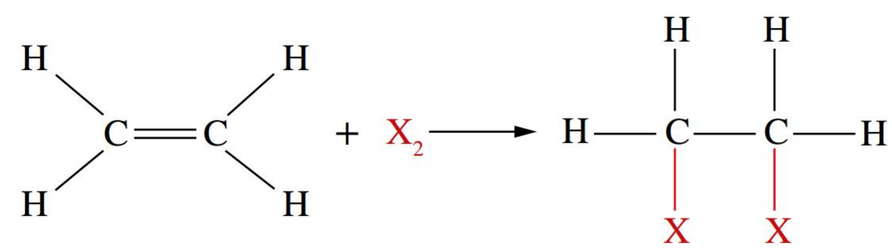


FIGURE 9.2.6 The addition reaction between an alkene and molecule X_2

> An addition reaction occurs when a small molecule is added to the double bond of the alkene, converting the double bond to a single bond.

When ethene reacts with a small molecule, each atom of the molecule forms a covalent bond to a carbon atom in the double bond. The double bond becomes a single bond. Unlike substitution reactions, there is no inorganic product formed. All the atoms in the reactants end up in the final product.

Four different types of addition reactions of alkenes are explained in detail below.

Reaction of alkenes with hydrogen—reduction of alkenes

Alkenes react with hydrogen gas in the presence of a metal catalyst, such as nickel, to form alkanes. This reaction converts an unsaturated molecule to a saturated one and is a redox reaction. As you have learnt in Unit 3, oxidation and reduction occur simultaneously in a redox reaction, the two processes involve loss (oxidation) and gain (reduction) of electrons of the two substances involved and one cannot occur without the other. However, in these organic pathways, we are focussing on the organic reactant, and thus we refer to whether it is undergoing oxidation or reduction – here, an alkene is reduced. The reaction shown in Figure 9.2.7 is the addition reaction of ethene and hydrogen gas to produce ethane.

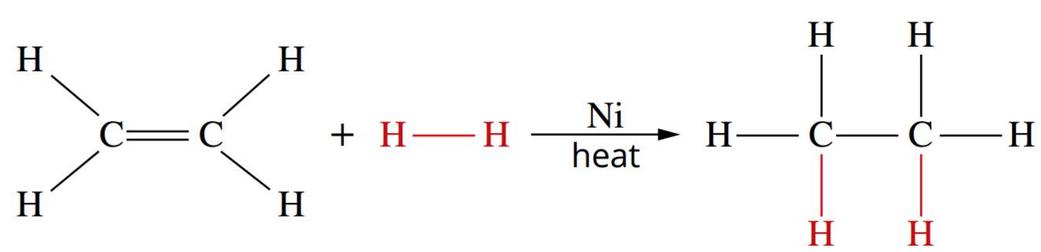


FIGURE 9.2.7 Addition reaction of ethene with hydrogen to form the corresponding saturated alkane, ethane

The activation energy for the reaction is too high for it to proceed at room temperature without a catalyst. Metals such as nickel, palladium and platinum are used as catalysts, and the reaction is usually heated. This reaction is a reduction reaction because hydrogen atoms are added and the oxidation state of the C atoms changes from –2 in ethene to –3 in ethane. Concurrently, hydrogen atoms are oxidised as the redox reaction occurs.

The triple bond in alkyne molecules can be converted to three single bonds by the addition of hydrogen atoms. This is also a reduction reaction – oxidation state of the C atoms changes from –1 in ethyne to –3 in ethane. Hydrogen atoms

are oxidised as the redox reaction occurs. It requires a strong metal catalyst and high temperatures to proceed. An example of an addition reaction of alkynes is the reduction of butyne:

$$CH_3{-}C{\equiv}C{-}CH_3 + 2H_2 \xrightarrow[\text{heat}]{\text{Ni}} CH_3{-}CH_2{-}CH_2{-}CH_3$$

Reaction of alkenes with halogens

Figure 9.2.8 shows the reaction of ethene with bromine to form 1,2-dibromoethane. The halogens add across the double bond of the molecule, so in the product, there is one bromine atom attached to each carbon atom.

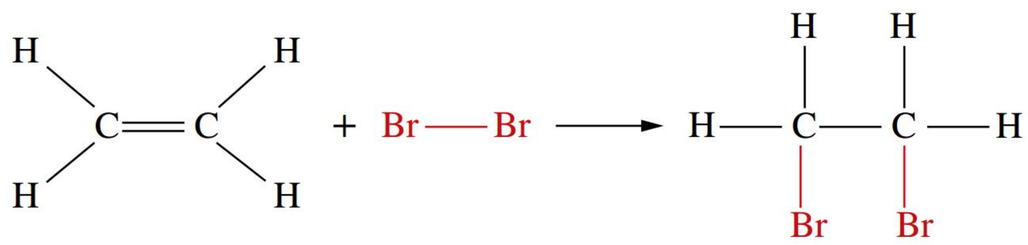


FIGURE 9.2.8 Addition reaction of ethene with bromine

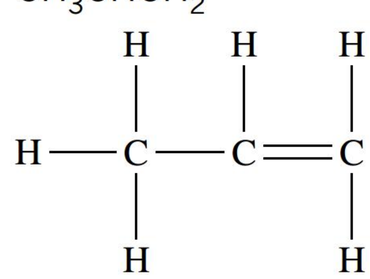
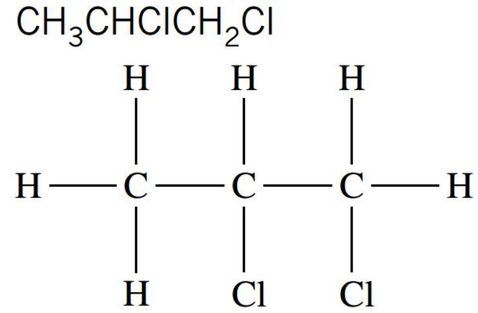
This reaction proceeds at room temperature without a catalyst. By identifying changes to oxidation states, we deduce that carbon atoms are oxidised and bromine atoms are reduced – a redox reaction is occurring. Other halogens such as Cl_2 and I_2 also undergo addition reactions with alkenes to form the corresponding di-substituted haloalkanes.

Bromine is often used as a test for the presence of a carbon–carbon double bond due to the ease and speed with which it reacts with an alkene. As described in Module 9.1, the brownish-red colour of the bromine quickly disappears when it is mixed with an alkene. Figure 9.2.9 demonstrates this test, showing the alkane in the test tube on the left and the alkene on the right. Note that the hydrocarbons are non-polar liquids and so are clearly visible as the upper layer in each test tube.

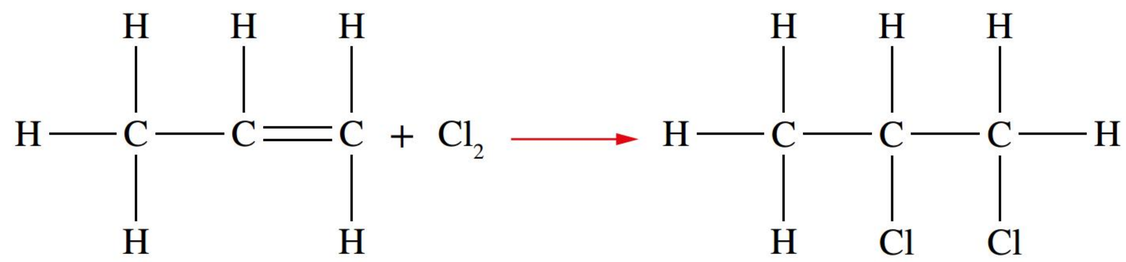
FIGURE 9.2.9 Immiscible layers of bromine water and alkane (left) and bromine water and alkene (right). This image shows the liquids re-separated after mixing. The alkene reacts with the coloured bromine and the solution loses colour (right). The test tube on the left shows that when an alkane is added to bromine water, no addition reaction occurs and so the colour of the dissolved bromine remains.

Worked example 9.2.2

DESCRIBING ADDITION REACTIONS OF ALKENES

Describe the addition reaction (also a reduction reaction) between propene and chlorine gas by constructing the chemical equation and structural formulas.	
Thinking	**Working**
Identify the alkene and double bond where addition will occur.	CH_3CHCH_2 
Identify the molecule to be added.	Cl_2
Deduce the product by adding a halogen to the two carbons of the double bond.	$CH_3CHClCH_2Cl$ 
Construct the chemical equation.	$CH_3CHCH_2 + Cl_2 \rightarrow CH_3CHClCH_2Cl$

Draw the structural formulas.



➤ Try yourself 9.2.2

DESCRIBING ADDITION REACTIONS OF ALKENES

Describe the addition reaction (also a reduction reaction) between but-1-ene and iodine gas by constructing the chemical equation and structural formulas.

Reactions of alkenes with water

Alkenes react with water under specific conditions to form the corresponding alcohol. For example, ethanol can be produced by an addition reaction of ethene and water, using an acid catalyst and heat to increase the rate of the reaction. Figure 9.2.10 shows the addition reaction of steam and ethene, using a phosphoric acid catalyst. This reaction is used extensively in industry for the production of ethanol.

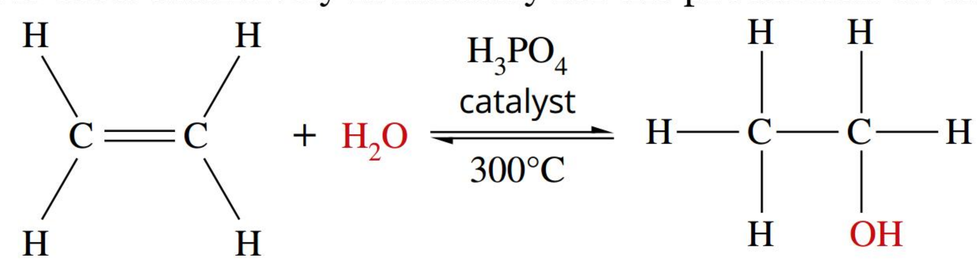


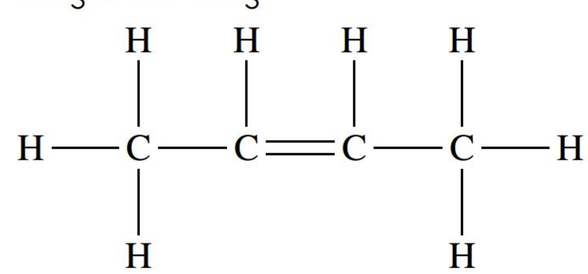
FIGURE 9.2.10 Addition reaction of ethene with water in the presence of a phosphoric acid catalyst and heat

The reaction is carried out at 300°C. The gaseous reactants are passed over a solid bed of the catalyst and gaseous ethanol is formed. In the addition reaction, water is 'added' across the double bond. The reaction is used for the commercial manufacture of ethanol because it is a one-step process that uses little energy, apart from initial heating. The heterogeneous (solid–gas) nature of the reaction system means it is easy for manufacturers to remove the product from the reaction mixture, leaving the catalyst intact.

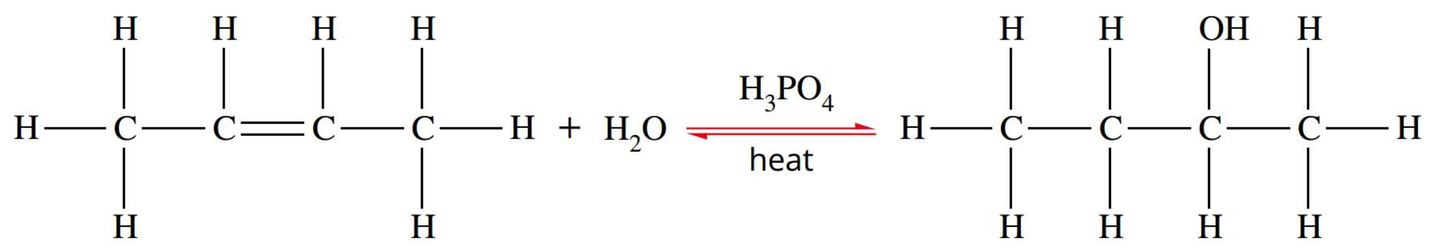
Worked example 9.2.3

DESCRIBING THE PRODUCTION OF ALCOHOL FROM AN ALKENE

Draw the structural formula of the alcohol produced by the reaction of water and but-2-ene.

Thinking	Working
Identify the organic reactant and double bond where addition occurs.	$CH_3CHCHCH_3$ 
Identify the inorganic reactant.	H_2O
Recall the addition reaction of but-2-ene and water (OH and H are added, one to each carbon atom of the double bond; reaction occurs in the presence of phosphoric acid and heat).	$CH_3CHCHCH_3 + H_2O \rightarrow CH_3CH_2CHOHCH_3$

Draw the structural formulas.



➤ Try yourself 9.2.3

DESCRIBING THE PRODUCTION OF ALCOHOL FROM AN ALKENE

Draw the structural formula of the alcohol produced by the reaction of water and ethene.

The production of an alcohol from an alkene is reversible using the same acid catalyst. The key idea here is that water is a reactant in the production of the alcohol. So, if we use heat and a concentrated acid catalyst as reaction conditions, we are using low water conditions. According to Le Chatelier principles, the equilibrium will favour the reactants side of the equation shown in Figure 9.2.10. In the presence of concentrated acid, an alkene is produced, whereas when water is present, an alcohol is produced. The effect of high/low water conditions also affects the production of esters via a condensation reaction (refer to Module 9.3).

Reactions of alkenes with hydrogen halides

Another small molecule that can be added across the double bond of an alkene is a hydrogen halide. For example, but-2-ene reacts with hydrogen chloride, a hydrogen halide, in an addition reaction. Figure 9.2.11 shows the reaction of but-2-ene with hydrogen chloride to produce a single product, 2-chlorobutane. In this reaction, a hydrogen atom adds to one of the carbon atoms in the carbon–carbon double bond and a halogen atom adds to the other carbon atom.

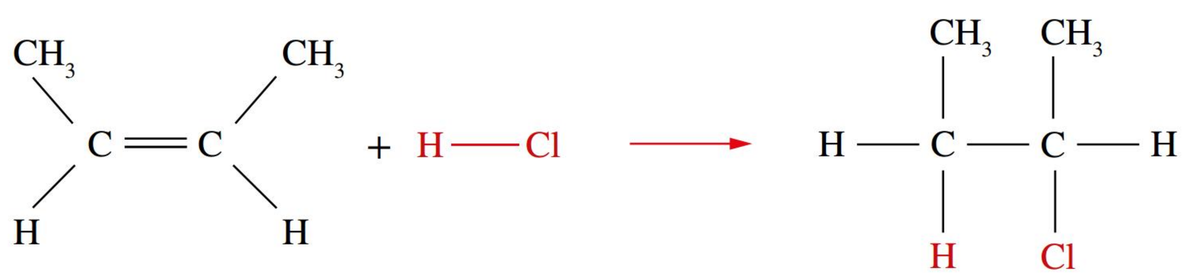


FIGURE 9.2.11 The addition reaction of but-2-ene with hydrogen chloride produces 2-chlorobutane.

However, as Figure 9.2.12 shows, when you react hydrogen chloride with an asymmetrical alkene such as but-1-ene, two products are possible.

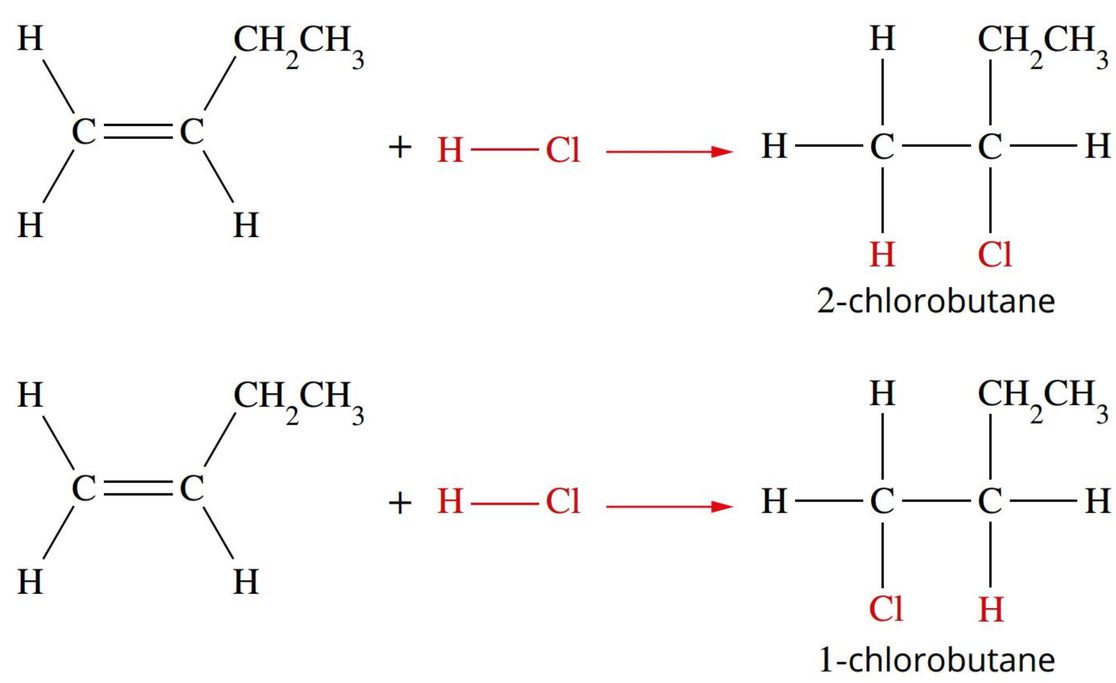


FIGURE 9.2.12 Addition reaction of but-1-ene with hydrogen chloride. Two isomers are possible as products

Markovnikov's rule states that, in the addition of HX or H_2O to an asymmetrical alkene, hydrogen adds to the carbon atom of the double bond that has the greater number of hydrogens attached.

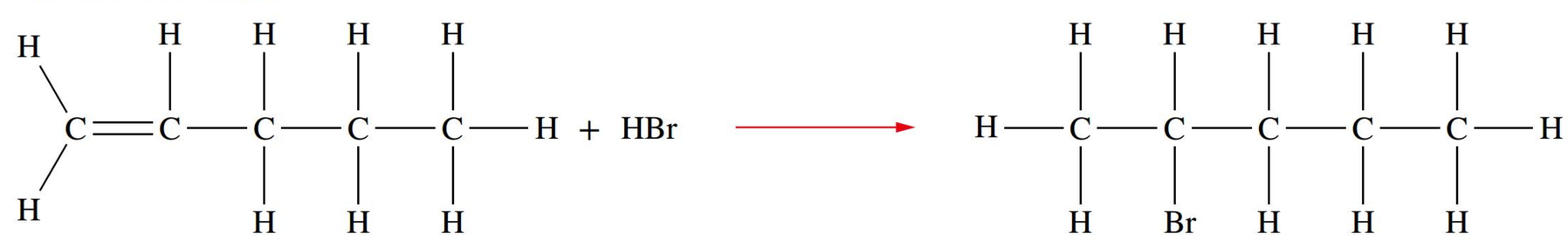
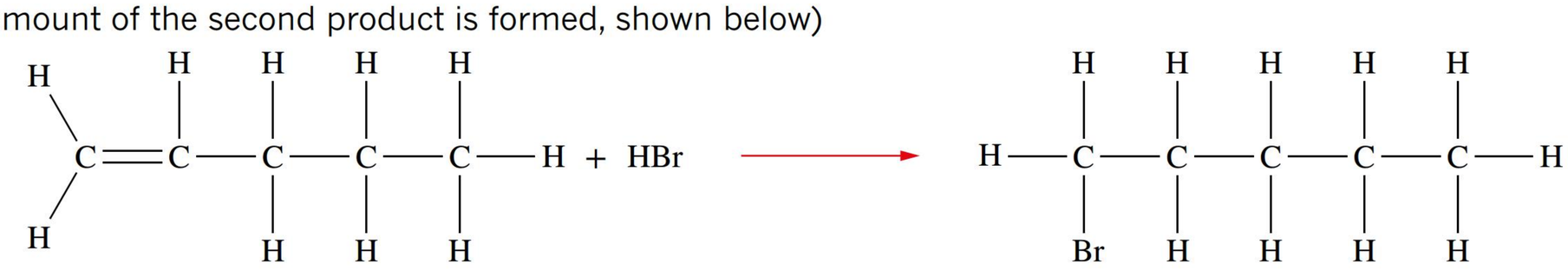
The addition reaction can produce two isomers. In one product, the hydrogen atom from the hydrogen chloride molecule has been added to the (C1) carbon atom in the carbon–carbon double bond at the end of the but-1-ene molecule. In the other product, the hydrogen atom has been added to the (C2) carbon atom at the other end of the carbon–carbon double bond.

When you react an asymmetrical alkene such as but-1-ene with an asymmetrical reactant, isomers are produced. More of one isomer is usually produced than the other. The greater formation of one isomer can be predicted using **Markovnikov's rule**. While it is important to be able to accurately determine which isomer is favoured, the mechanism is outside the scope of the syllabus.

Markovnikov's rule states that, during the addition of HX or H_2O to an asymmetrical alkene, hydrogen adds to the carbon atom of the double bond that has the greater number of hydrogens attached. In Figure 9.2.12, as the double bond between carbon number 1 and carbon number 2 becomes a single bond, atoms are added to both carbon number 1 and carbon number 2. However, carbon number 1 has two hydrogen atoms compared to the single hydrogen atom attached to the carbon number 2; therefore, the hydrogen will add to carbon number 1. This means that the other atom, the halogen, must be added to carbon number 2. Then, the main product of the addition of HCl to but-1-ene will be 2-chlorobutane (Figure 9.2.12 top isomer), not 1-chlorobutane (Figure 9.2.12 lower isomer).

Worked example 9.2.4

USING MARKOVNIKOV'S RULE TO IDENTIFY THE PRODUCTS OF ADDITION TO AN ASYMMETRICAL ALKENE

Describe the reaction and products of the addition reaction of pent-1-ene with hydrogen bromide.	
Thinking	**Working**
Identify the organic molecule containing a double bond.	$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$ C C C C C 1 2 3 4 5
Identify the small molecule to be added.	HBr
Identify the number of hydrogen atoms attached to each carbon atom at the double bond (carbon number 1 and carbon number 2), and determine which carbon atom has the most hydrogens.	Carbon number 1 has two hydrogen atoms, while carbon number 2 has one hydrogen atom.
Add the hydrogen atom of HBr to the carbon with the most hydrogens (carbon number 1), and the bromine atom from the HBr to the other carbon (Markovnikov's rule).	Hydrogen adds mostly to carbon number 1 and adds to carbon number 2 to a very slight extent. Bromine adds mostly to carbon number 2 and adds to carbon number 1 to a very slight extent. $CH_3CHBrCH_2CH_2CH_3$ is mostly produced.
Construct the reaction equation.	$CH_2CHCH_2CH_2CH_3 + HBr \rightarrow CH_3CHBrCH_2CH_2CH_3$ (smaller amount of $CH_2BrCH_2CH_2CH_2CH_3$ produced)
Draw the structural formulas.  (a small amount of the second product is formed, shown below) 	

➤ Try yourself 9.2.4

USING MARKOVNIKOV'S RULE TO IDENTIFY THE PRODUCTS OF ADDITION TO AN ASYMMETRICAL ALKENE

Describe the reaction and products of the addition reaction of 2-methylbut-2-ene with hydrogen chloride.

Addition reactions of alkenes to form poly(alkenes)

Polyethene is an example of a **polymer** ('many units'). Polymers are very long molecules formed from the linking of a large number of small molecules, called **monomers** ('one unit'). Polyethene is formed from the reaction of thousands of ethene monomer molecules. The reaction, shown in Figure 9.2.13, is an example of an **addition polymerisation** process. Several thousand ethene monomers usually react to make one molecule of polyethene. Large square brackets around the repeating unit, and the subscript *n*, are used to simplify the drawing of long polymer molecules. The value of *n* varies with each polymer molecule but the average molecular chain formed may contain around 20 000 carbon atoms. Reaction conditions also vary with the polymer type, catalysts are often required.

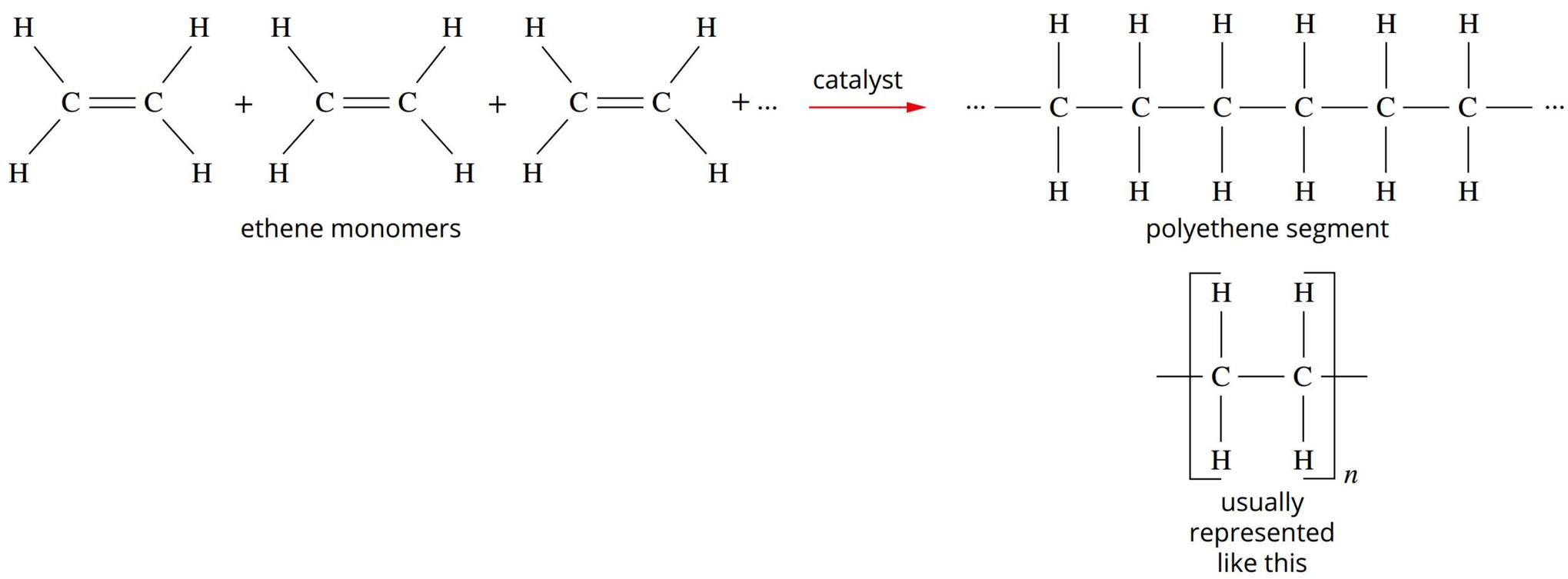


FIGURE 9.2.13 Thousands of ethene monomers can join in an addition reaction to make one chain of polyethene. The standard notation shown on the right simplifies the drawing of such a large chain.

Note that the empirical formula of each monomer is the same as that of the polymer, since there are no other products in addition polymerisation reactions. When ethene polymerises, the double bonds break and new covalent bonds are formed between carbon atoms on nearby monomers. The polyethene formed does not contain any double bonds. The addition polymerisation reaction can involve any number of monomers and is described as follows:

$$n(CH_2{=}CH_2) \rightarrow [{-}CH_2{-}CH_2{-}]n$$

Other alkenes react in a similar way. For example, propene ($CH_2{=}CH{-}CH_3$) forms polypropene ($[{-}CH_2{-}CH_2{-}CH_2{-}]n$) and butene ($CH_2{=}CH{-}CH_2{-}CH_3$) forms polybutene ($[{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}]n$). Polymers are further explained in Chapter XX.

ELIMINATION REACTIONS OF HALOALKANES

Addition reactions can be reversed. This reaction is called an elimination reaction because the haloalkane loses two atoms (one hydrogen and one halogen) and regains a double bond – there is an extra product because atoms have been removed from the haloalkane. We described the addition reaction as reduction of the organic molecule, and so reversal of addition, known as elimination, is designated as oxidation of the organic molecule. The elimination reaction of chloroethane is shown in Figure 9.2.14.

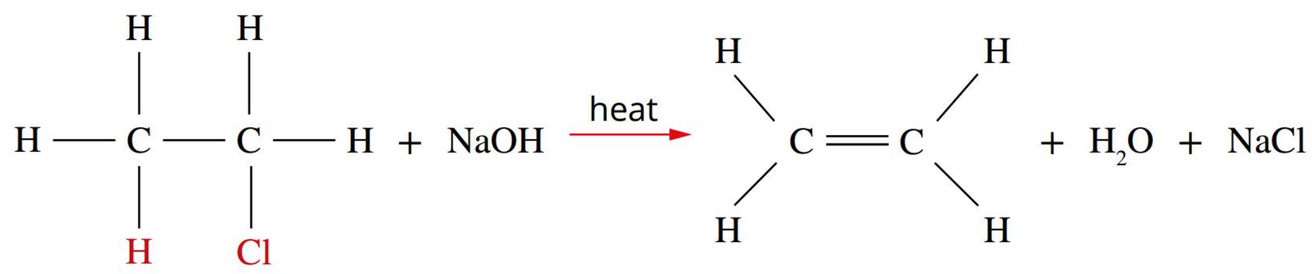


FIGURE 9.2.14 Reaction of chloroethane with sodium hydroxide to give ethene

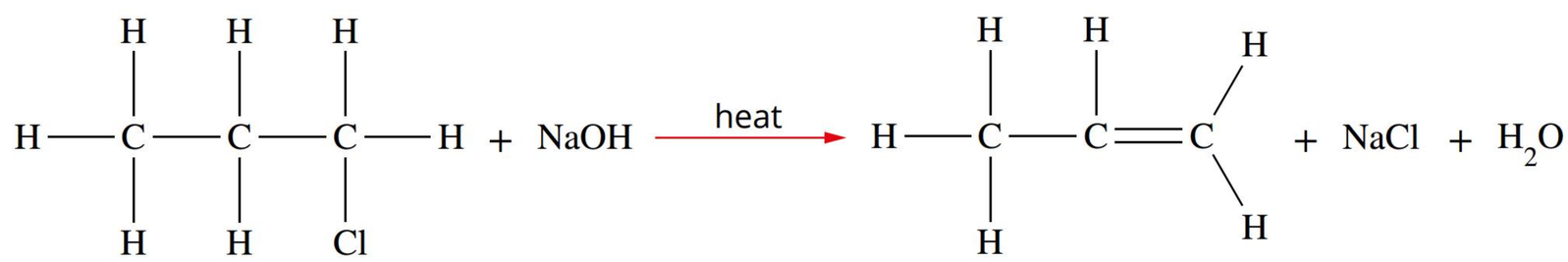
In elimination reactions, a hydrogen is removed from one carbon atom and a halogen is removed from another carbon atom and an unsaturated molecule is produced from a saturated molecule. This reaction requires a strong base such as sodium hydroxide and heat to proceed. Reaction conditions of elimination reactions are important because milder conditions, such as lower temperatures, will favour a substitution reaction (discussed earlier in the module).

Worked example 9.2.5

PRODUCTS OF AN ELIMINATION REACTION OF A HALOALKANE USING SODIUM HYDROXIDE

Complete a structural equation to identify the products of an elimination reaction of 1-chloropropane and sodium hydroxide.

Thinking	Working
Identify the reactants in the reaction.	$CH_3CH_2CH_2Cl$ and NaOH
Recall the elimination process (at high temperature) and identify the adjacent carbon atoms that each lose an atom. A Cl atom and an H atom are removed. Water and NaCl are produced.	$CH_3CH_2CH_2Cl + NaOH \rightarrow CH_3CHCH_2 + NaCl + H_2O$
Draw the structural formulas.	



➤ Try yourself 9.2.5

PRODUCTS OF AN ELIMINATION REACTION OF A HALOALKANE USING SODIUM HYDROXIDE

Complete a structural equation to identify the products of an elimination reaction of 1-bromobutane and sodium hydroxide.

9.2 Review

SUMMARY

- Alkanes and alkenes burn in the presence of oxygen to produce carbon dioxide and water (redox reaction).
- Alkanes are generally unreactive but they can undergo substitution reactions with halogens in the presence of UV light to produce haloalkanes.

- Haloalkanes undergo substitution reactions with:
  - haloalkanes to produce a different haloalkane or a dihaloalkane
  - ammonia to produce amines
  - sodium hydroxide at low temperature to produce alcohol and a salt.
- Alkenes are unsaturated hydrocarbons. They undergo addition reactions to produce one product – a saturated compound.
- Alkenes undergo addition reactions with:
  - hydrogen and a metal catalyst to produce alkanes (this reaction is also known as a reduction reaction)
  - halogens to produce dihaloalkanes
  - water and a phosphoric acid catalyst at high temperature to produce alcohols
  - hydrogen halides to produce haloalkanes. Under typical conditions, asymmetrical alkenes mostly add the hydrogen to the carbon that already has more hydrogen atoms (Markovnikov's rule). A small amount of the alternate product is formed.
- A change in the oxidation state of an atom during a reaction indicates that oxidation or reduction has taken place. A redox reaction requires both oxidation and reduction. Key redox reactions are addition of H_2 and X_2 to alkenes and combustion of alkanes.
- The addition of a hydrogen halide to an alkene can be reversed using a strong base such as sodium hydroxide under specific conditions such as high temperature and low water conditions – this is called an elimination reaction.
- Both substitution and elimination reactions involve the removal of small molecules from the original molecule, thus producing more than one product.
- Alkenes often require a catalyst to undergo addition polymerisation reactions to form large polymer molecules composed of carbon–carbon single bonds.

KEY QUESTIONS

Describe

1 State the products of the following reaction and balance the chemical equation:

$C_2H_4(g) + 3O_2(g) \rightarrow$ ..... (g) + ... (g)

2 Name the product formed when ethene reacts with each of the following:

a hydrogen chloride
b chlorine
c water in the presence of phosphoric acid catalyst and heat
d hydrogen in the presence of a metal catalyst and heat.

3 Name the most likely organic product formed when each of the following pairs of compounds react.

a bromoethane and ammonia
b 2-chlorobutane and sodium hydroxide at high temperature
c pent-1-ene and water in the presence of a strong acid catalyst

4 Construct a balanced chemical equation to show the complete combustion of the following alkanes. Remember to include the states of the reactants and products.

a gaseous methane **b** liquid hexane

Apply

5 Represent each of the following reactions with a balanced chemical equation and molecular formulas.

a gaseous propene bubbled into bromine solution
b gaseous but-2-ene reacted with steam in the presence of a phosphoric acid catalyst

6 Construct balanced equations to represent all stages in the formation of carbon tetrachloride from methane and chlorine.

7 Use structural formulas to construct equations and name the products of the reactions of:

a but-1-ene with chlorine
b but-2-ene with hydrogen bromide.

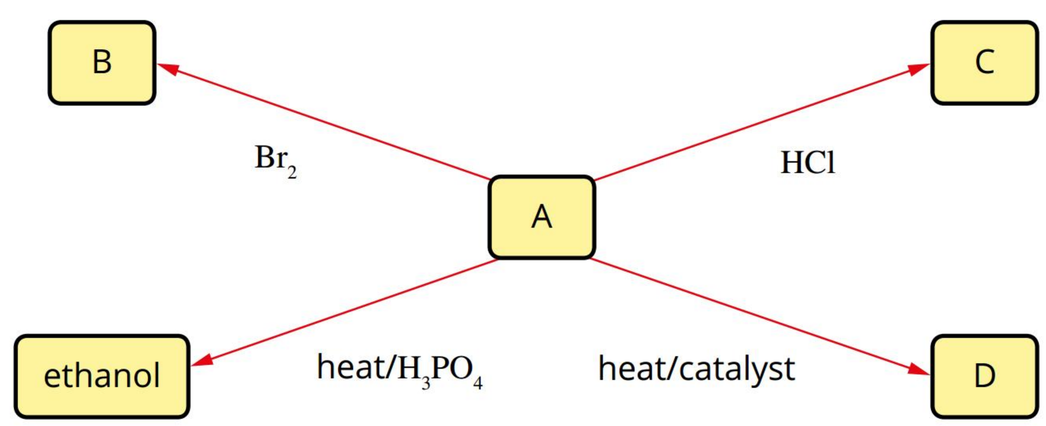
8 Explain the difference in reactivity of alkenes and alkanes with bromine water.

9 State the two possible reaction products when but-1-ene is heated with phosphoric acid and water and explain why they are not produced in equal amounts.

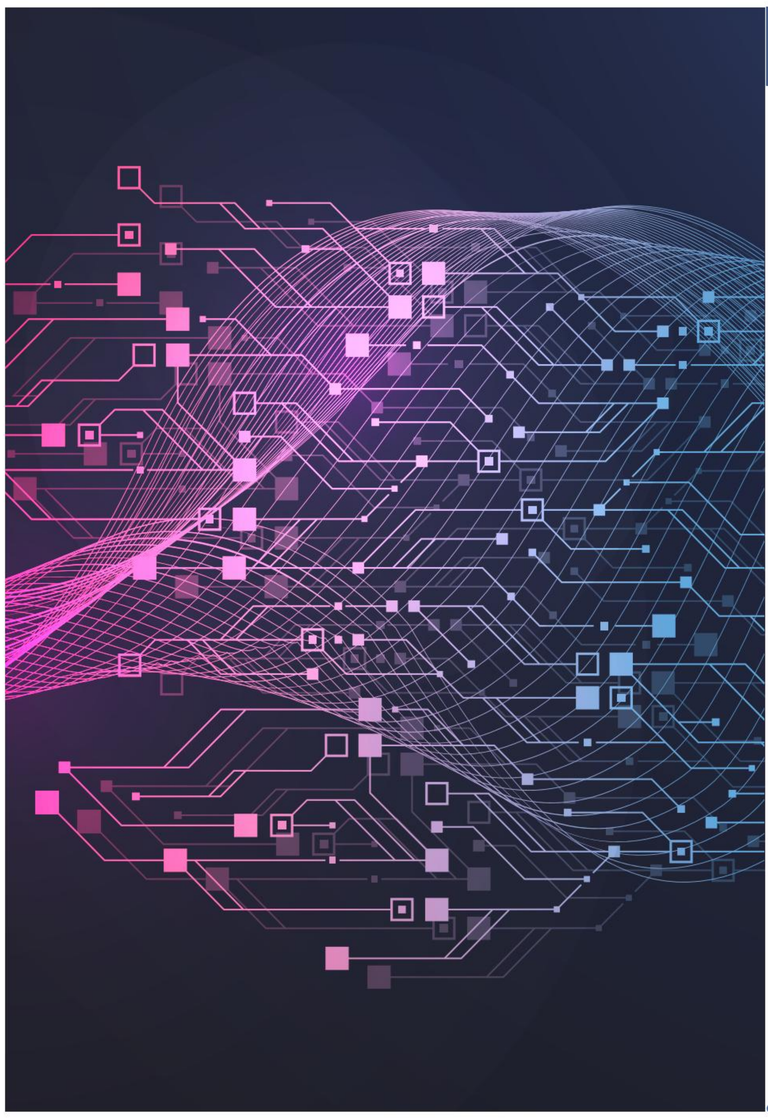
10 Use structural formulas to construct an equation and name the products for the reaction of hexane and bromine gas in UV light (assuming a single molecule of bromine reacts).

Analyse

11 Name A–D using the information shown in the reaction diagram below.



9.3 Reactions of compounds containing oxygen and nitrogen atoms



BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that oxidation of primary, secondary or tertiary alcohols results in different products depending on the position of the hydroxyl group (Reactions 1, 2 and 3)
- predict and identify the products of oxidation of alcohols from the alcohol type
- explain that combustion is another oxidation reaction of alcohols
- describe and explain that carboxylic acids undergo a condensation reaction with alcohols in the presence of an acid catalyst to produce esters (Reaction 4)
- identify the products of ester hydrolysis (Reaction 5)
- recognise that a condensation reaction occurs when a carboxylic acid reacts with an amine to form an amide (Reaction 6)
- explain organic chemistry reactions using chemical equations and structural formulas
- understand conditions and catalysts necessary for certain reactions
- describe how molecules containing oxygen and nitrogen are part of organic chemistry reaction pathways.

In Module 9.2, you saw simple organic molecules, such as alkanes, converted by substitution and addition reactions to more complex molecules containing oxygen and nitrogen atoms. Important examples of these products are alcohols and amines. These molecules can undergo further chemical change, often increasing the complexity and chemical reactivity of their structures. Aldehydes, ketones, carboxylic acids, esters and amides, described in this module, are produced in this way. Eventually, after many reactions, much larger, biologically important molecules such as triglycerides and proteins are produced. The three key reactions explained in this module are oxidation, condensation and hydrolysis. These reactions are introduced in Figure 9.3.1.

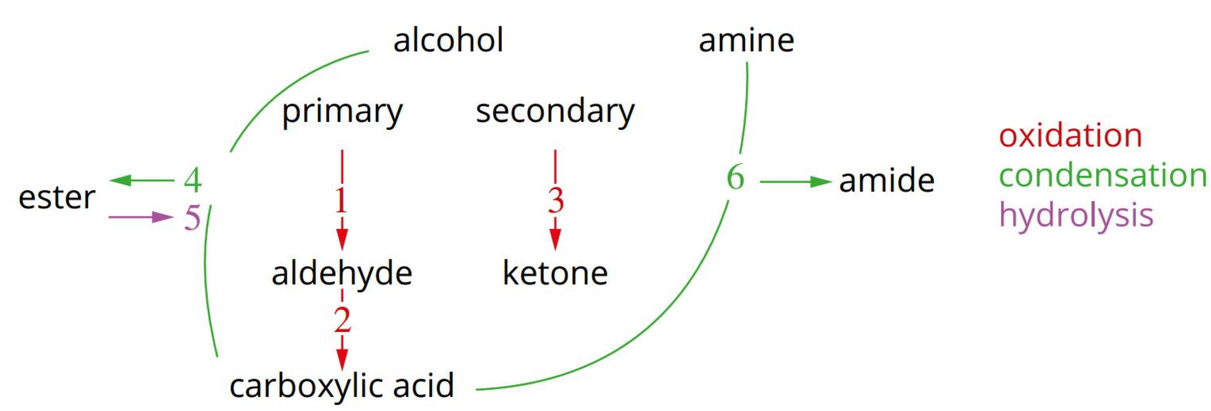


FIGURE 9.3.1 Overview of reaction pathways for compounds containing oxygen and nitrogen. Coloured numbers indicate the type of reaction—oxidation reactions are red, condensation reactions are green and hydrolysis reactions are purple.

Molecules containing oxygen and nitrogen are part of organic chemistry reaction pathways, as shown in Figure 9.3.2.

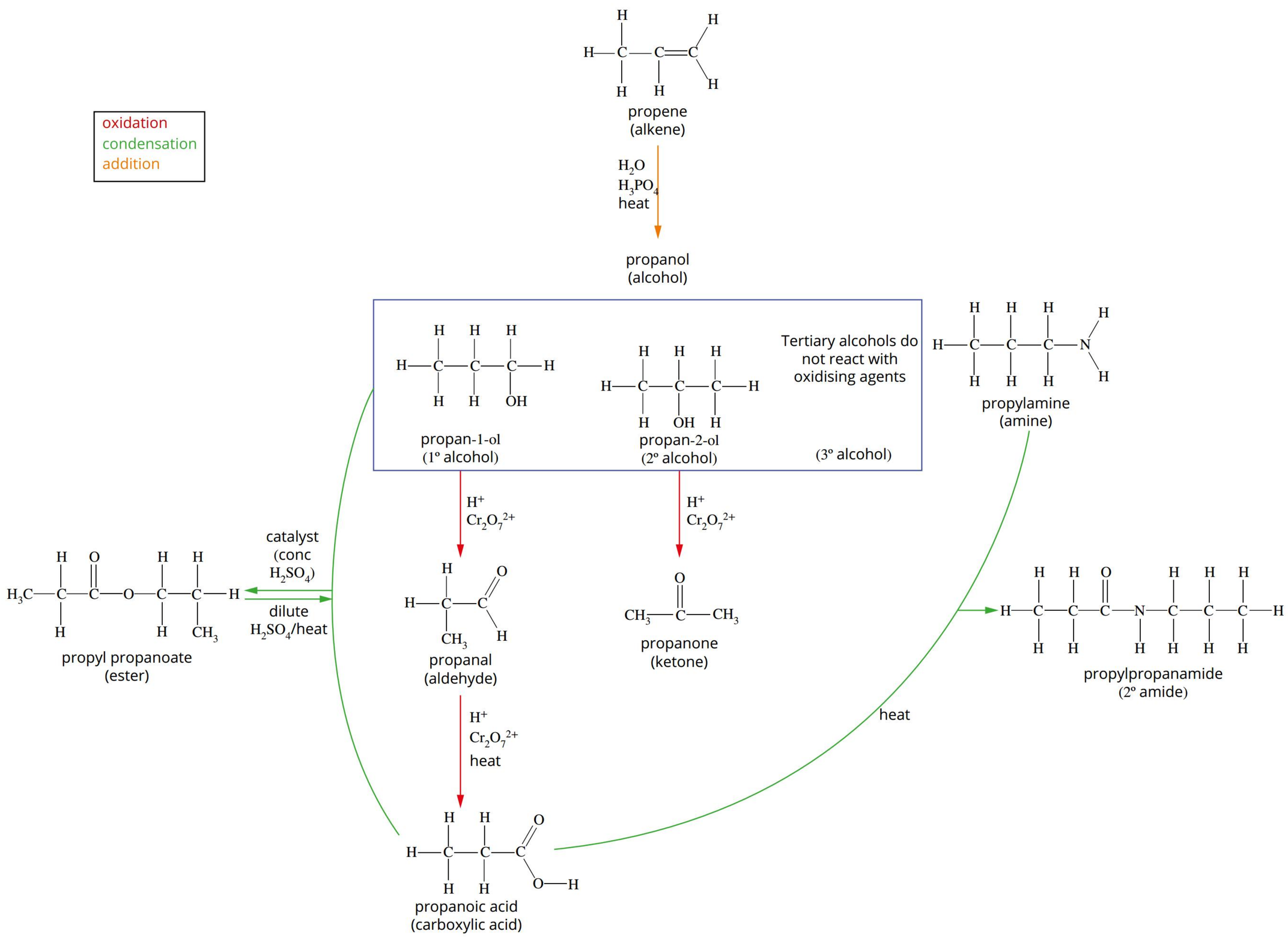


FIGURE 9.3.2 Organic chemistry reactions described in this module

OXIDATION REACTIONS OF ALCOHOLS

In Module 9.2, you learnt that alcohols can be produced by addition reactions of alkenes or by a substitution reaction of a haloalkane. The hydroxyl functional group gives the molecule different properties from the alkene or haloalkane from which it was made. These differences relate directly to the charge imbalances in the molecule generated by changes to its structure and polarity of its covalent bonds.

In this module, you will examine the common oxidation reactions of alcohols. Oxidation and reduction occur simultaneously, and you will remember that these reactions are redox reactions – describing the loss of electrons by one substance and the gain of electrons by another. When we focus on the organic reactant, we refer to whether it is undergoing oxidation or reduction. This means that when we describe 'oxidation of alcohols', we recognise reduction must also be occurring for another molecule. We can identify this molecule because, as learnt in Unit 3, an increase in the oxidation number of an atom is evidence of oxidation occurring, whereas a decrease in oxidation number indicates reduction has occurred.

When relating to organic reactions, we can restate the oxidation and reduction definitions as:

- oxidation is the gain of oxygen or the loss of hydrogen
- reduction is the gain of hydrogen or the loss of oxygen.

By using these rules, you can quickly identify oxidation and reduction in a range of organic chemistry reactions.

To understand reactions of alcohols, you will need to remember the types of alcohols you learnt about in Module 8.4. Alcohols are classified into three types: primary, secondary and tertiary. The type depends on the position of the hydroxyl group within the molecule. The variation of the hydroxyl group makes the alcohols structural isomers of each other.

- Primary alcohols are alcohols in which the –OH group is bonded to a carbon that is attached to only one alkyl group. This carbon is also known as the primary carbon. These alcohols first oxidise to form aldehydes and then further oxidise to form the corresponding carboxylic acids.
- Secondary alcohols are alcohols in which the –OH group is bonded to a carbon that is bonded to two alkyl groups. This carbon is also known as the secondary carbon. These alcohols oxidise to form ketones.
- Tertiary alcohols are alcohols in which the –OH group is bonded to a carbon that is bonded to three alkyl groups. This carbon is also known as the tertiary carbon. These alcohols are resistant to oxidation by inorganic oxidising agents and will not normally react.

Figure 9.3.3 shows how the different isomers of butanol can be classified as primary, secondary or tertiary alcohols. Chemists often use the symbols 1°, 2° and 3° as a shorthand way of indicating whether an alcohol is primary, secondary or tertiary, respectively.

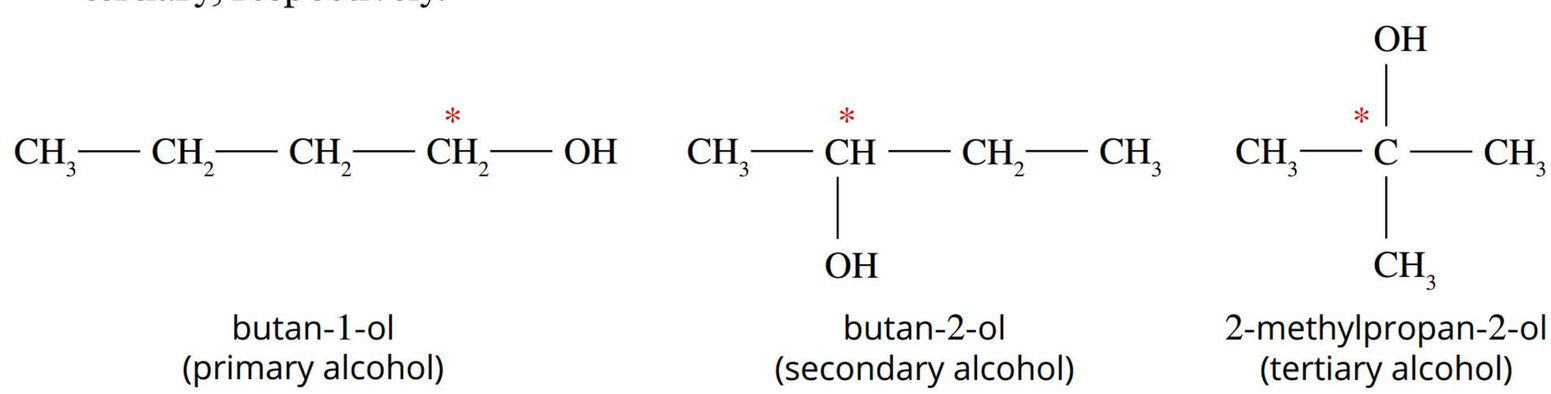


FIGURE 9.3.3 Structures of some primary (1°), secondary (2°) and tertiary (3°) alcohols. The asterisk identifies the carbon atom that determines the 1°, 2° or 3° nature of the alcohol.

Combustion of alcohols

Alcohols react with oxygen to produce carbon dioxide and water while releasing significant amounts of energy. It is an **exothermic** oxidation–reduction reaction. If the supply of oxygen is plentiful, the products of combustion will be carbon dioxide and water. This is known as complete combustion. Combustion is an oxidation reaction because both the hydrogen and carbon atoms in the reactant become associated with oxygen as small molecules (CO_2 and H_2O) in the products. This agrees with our definition of oxidation as 'adding oxygen'. The chemical equation for combustion of ethanol is written as:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

Further evidence for this reaction being an oxidation comes from the oxidation number of the carbon atom – we can see that the oxidation number of carbon in CO_2 is +4, whereas its oxidation number in C_2H_5OH is –2.

Ethanol (methylated spirits), which contains about 95% ethanol, is used as a fuel for camping stoves. A 70% ethanol solution is used in microbiological techniques to sterilise instruments.

Oxidation of alcohols

The second oxidation reaction type discussed here involves alcohols and is mediated by strong inorganic oxidising agents such as acidified solutions of potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$). The products of these oxidation reactions depend on the type of alcohol involved.

Oxidation of primary alcohols

A primary alcohol can be oxidised to a carboxylic acid in two stages, as shown in Figure 9.3.4. The reaction requires an oxidising agent such as acidified potassium

dichromate ($K_2Cr_2O_7$) or acidified potassium permanganate ($KMnO_4$). As we have seen, oxidation 'adds oxygen' or 'removes hydrogen', and during the oxidation of primary alcohols, both reactions occur. In the first stage, the primary alcohol is oxidised to an aldehyde by the removal of two hydrogen atoms. In the second stage, further heating of the reaction mixture in the presence of the oxidising agent oxidises the aldehyde to a carboxylic acid by the addition of an oxygen atom. Alcohols and aldehydes have relatively low boiling points and so a **reflux** setup returns boiled liquid back to the reacting phase. As shown in Figure 9.3.5, vapourised alcohol or aldehyde is returned to the reaction flask by cooling within the water jacket of a condenser. The liquid in the reaction mixture remains at its boiling point.

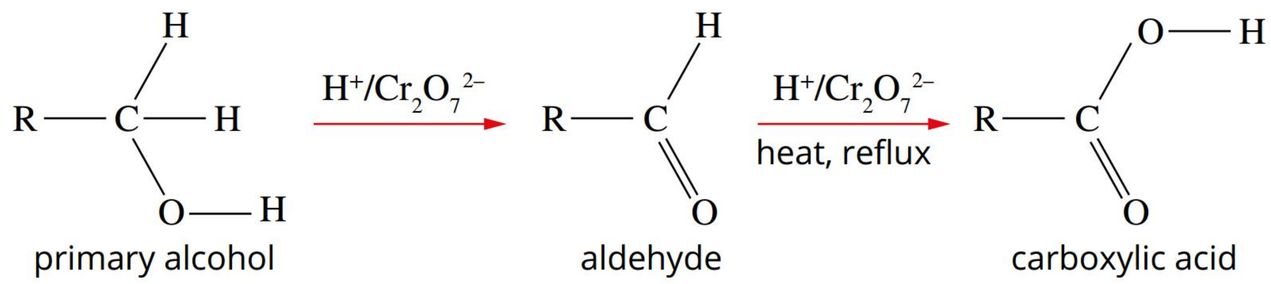


FIGURE 9.3.4 General equation for the two stages of the oxidation of a primary alcohol. The R groups in the structures represent alkyl groups.

FIGURE 9.3.5 Laboratory equipment used for heating and active reflux during the oxidation of an alcohol to a carboxylic acid.

> **Stage 1 in the oxidation of primary alcohols removes two hydrogen atoms from the alcohol structure and produces an aldehyde.**
>
> **Stage 2 in the oxidation of primary alcohols adds an oxygen atom to the aldehyde structure and produces a carboxylic acid.**

An example of oxidation of a primary alcohol is shown in Figure 9.3.6. It shows that propan-1-ol is first oxidised to propanal (an aldehyde) and then oxidised to propanoic acid (a carboxylic acid).

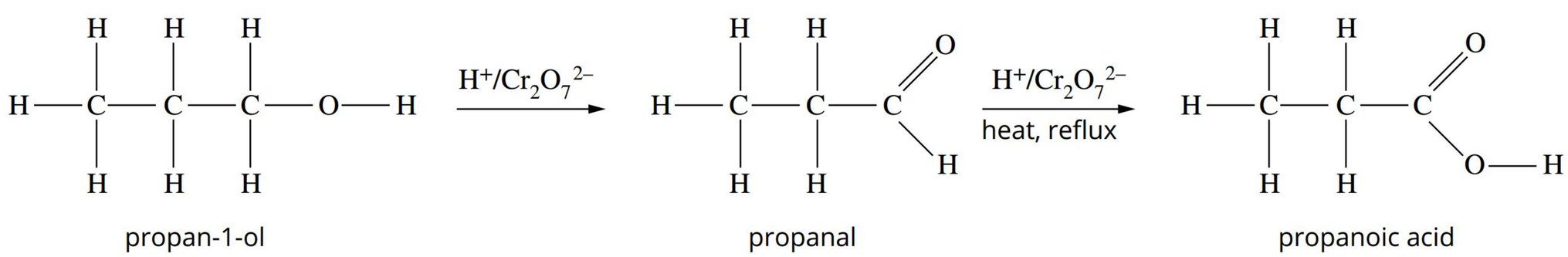


FIGURE 9.3.6 Equations for the oxidation of the primary alcohol propan-1-ol showing structural formulas. In the first oxidation, two hydrogen atoms are removed. In the second oxidation, an oxygen atom is gained.

If the desired product is an aldehyde rather than a carboxylic acid, milder conditions (lower temperatures and shorter reaction times) must be used, and the aldehyde is distilled from the reaction mixture as it forms to prevent further oxidation. Higher temperatures, reflux and longer reaction times favour the formation of the carboxylic acid over the aldehyde.

> **Aldehydes are produced as an intermediate in the oxidation of a primary alcohol to a carboxylic acid. If an aldehyde is the desired product, milder temperature conditions must be used, and the aldehyde product should be removed by distillation as it forms. Continued heating under reflux results in a carboxylic acid.**

Oxidation of secondary alcohols

When secondary alcohols are oxidised by strong oxidising agents such as solutions of acidified potassium dichromate or acidified potassium permanganate, the corresponding ketones are produced. This agrees with our definition of oxidation as 'removing hydrogen' because the –OH group becomes a =O bond, and the carbon atom also loses a hydrogen atom. Figure 9.3.7 gives the general equation for the oxidation of secondary alcohols to ketones.

> **Oxidation of secondary alcohols to ketones removes two hydrogen atoms from the alcohol structure.**

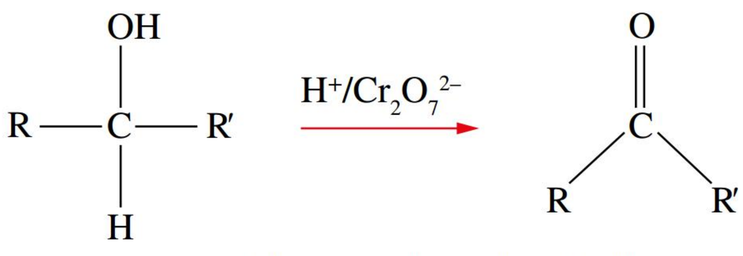


FIGURE 9.3.7 The general equation for the oxidation of a secondary alcohol

Figure 9.3.8 gives the equation for the production of the ketone propanone by the oxidation of the secondary alcohol propan-2-ol.

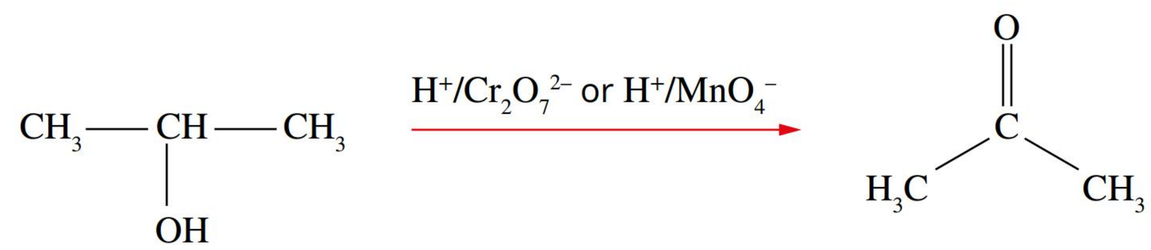
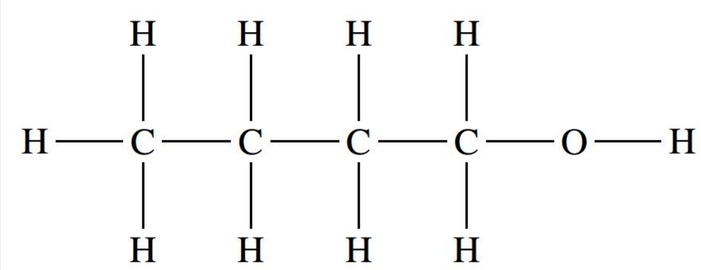
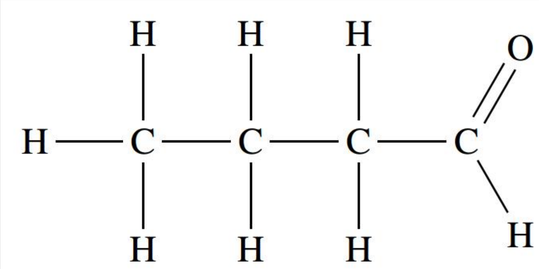
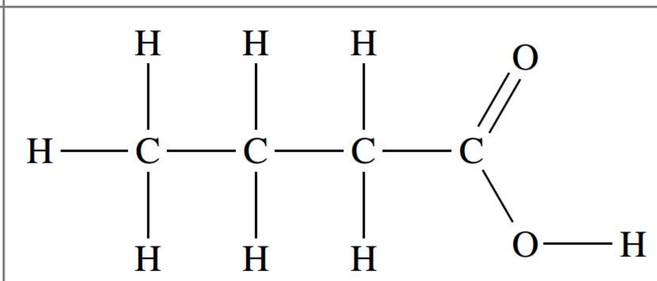


FIGURE 9.3.8 The secondary alcohol propan-2-ol can be oxidised to propan-2-one

Worked example 9.3.1

IDENTIFYING AND DESCRIBING A REACTION OF AN ORGANIC ALCOHOL

Identify the name of the reaction and draw the product(s) formed when butanol is heated with acidified potassium dichromate.

Thinking	Working
Recall that butanol has four carbon atoms and an OH functional group on the first carbon (when no number is specified, we assume carbon one contains the functional group).	
Use the organic reaction pathways in Figure 9.3.6 on page 373 to recall that a primary alcohol will be first oxidised by acidified potassium dichromate to an aldehyde.	Butanol will be oxidised to butanal.
Butanal has a C=O functional group formed by the loss of two hydrogen atoms from butanol. Draw the structure of butanal.	
Use the organic reaction pathways in Figure 9.3.6 on page 373 to recall that aldehyde will be further oxidised, with heating under reflux and acidified oxidising agent to a carboxylic acid.	Butanal will be oxidised to butanoic acid.
The second oxidation adds an oxygen atom and so the CHO group becomes COOH. Draw the structure of butanoic acid.	

➤ Try yourself 9.3.1

IDENTIFYING AND DESCRIBING A REACTION OF AN ORGANIC ALCOHOL

Identify the name of the reaction and draw the product(s) formed when butan-2-ol is heated with acidified potassium dichromate.

Tertiary alcohols and oxidising agents

During the oxidation of alcohols, there is a C=O bond formed and a simultaneous decrease (at the same carbon atom) in the number of C–H bonds. However, tertiary alcohols are resistant to reaction with solutions of acidified potassium dichromate or potassium permanganate because the carbon attached to the hydroxyl group does

not have a C–H bond to break, so oxidation cannot occur at that carbon atom. As a result, tertiary alcohols cannot normally be oxidised by heating in the presence of a strong oxidant such as acidified dichromate or acidified permanganate. The primary and secondary alcohols have at least one hydrogen atom at the carbon being oxidised and so a C=O bond can form in this position.

Colour changes in oxidation reactions

In Module 9.1, you learnt that some organic compounds can be identified using colour change reactions. The strong oxidising agents potassium dichromate and potassium permanganate are both highly coloured due to the presence of the transition elements chromium (Cr) and manganese (Mn).

A solution of dichromate ions in water is orange in colour. When this acidified dichromate solution is used to oxidise a primary or secondary alcohol, the chromium (VI) in the dichromate is reduced to the Cr^{3+} ion, which is green in colour. This colour change from orange to green can be used as a qualitative test to indicate that oxidation of an organic compound has taken place. The colour changes observed for the reaction of primary, secondary and tertiary alcohols with potassium dichromate are shown in Figure 9.3.9.

A solution of acidified potassium permanganate reagent is deep purple in colour. When this solution reacts with primary or secondary alcohols, the manganese (VII) in the permanganate ion (MnO_4^-) is reduced to Mn^{2+}, which is colourless. Tertiary alcohols do not react, so there is no change in the colour of the solution, as shown in Figure 9.3.10.

Primary alcohols are oxidised partially to aldehydes or fully to carboxylic acids using an acidified oxidising agent and heat. The aldehyde is removed by distillation after production or retained (using reflux and continued heating) for further oxidation to a carboxylic acid.

Secondary alcohols are oxidised to ketones using an acidified oxidising agent and heat.

Tertiary alcohols cannot be oxidised.

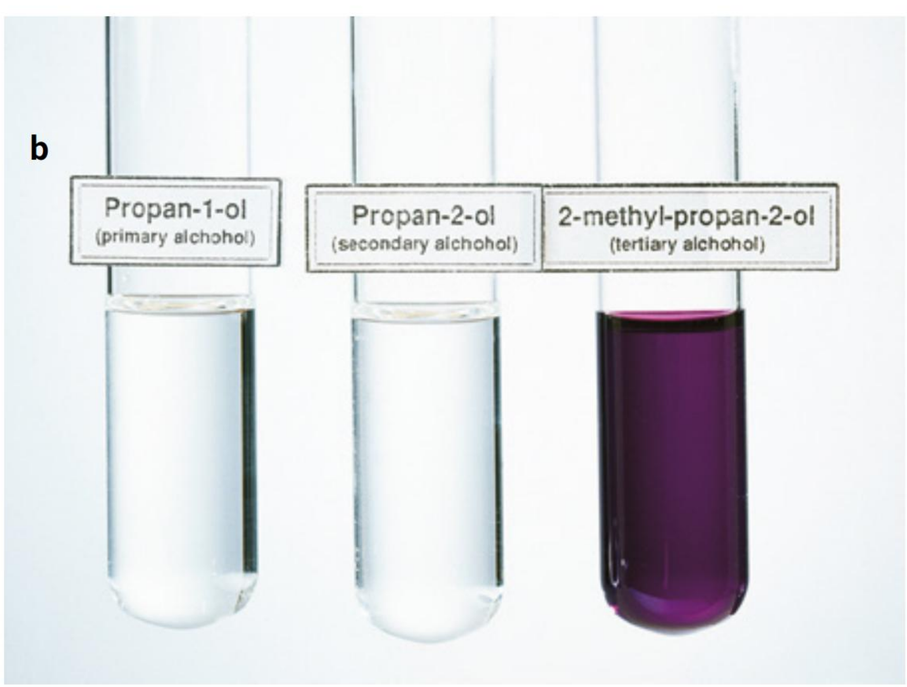


FIGURE 9.3.10 (a) The strong oxidising agent potassium permanganate is deep purple in colour. (b) On reaction with primary and secondary alcohols, the colour changes from purple to colourless. The tertiary alcohol is resistant to oxidation under these conditions and does not react, and so the solution does not change colour.

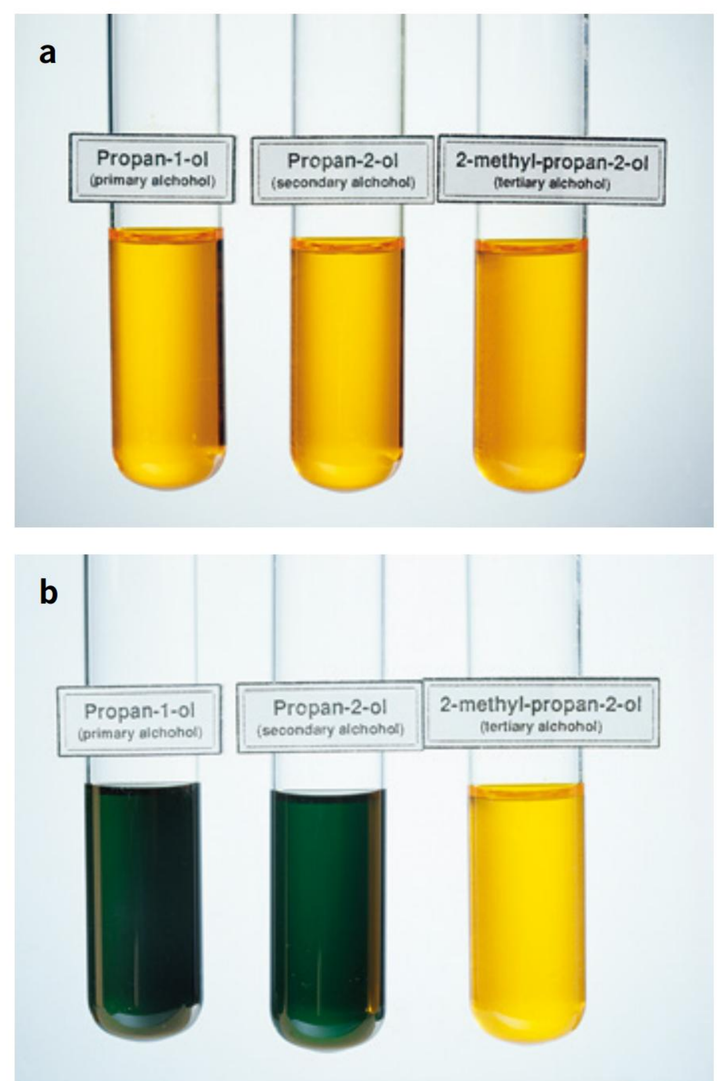


FIGURE 9.3.9 (a) Acidified potassium dichromate has an orange colour prior to reacting with alcohols. (b) Solutions of the primary alcohol propan-1-ol and secondary alcohol propan-2-ol with acidified potassium dichromate change from orange to green on heating. Tertiary alcohols such as 2-methylpropan-2-ol will not react under these conditions, so no colour change is observed.

Table 9.3.1 summarises the reactions of primary, secondary and tertiary alcohols with an acidified solution containing dichromate or permanganate ions.

TABLE 9.3.1 Summary of the oxidation reactions of primary, secondary and tertiary alcohols with acidified dichromate solution or acidified permanganate solution

Type of alcohol	Products	Colour change of acidified potassium dichromate solution	Colour change of acidified potassium permanganate solution
primary (1°)	mild conditions and immediate distillation (removal) of products produces aldehydes; higher temperatures and longer reaction times under reflux produces carboxylic acids	orange to green	purple to colourless
secondary (2°)	ketones	orange to green	purple to colourless
tertiary (3°)	no products because tertiary alcohols are resistant to oxidation by these oxidising agents	no change—solution stays orange	no change—solution stays purple

Reactions that involve the combination of two reactants and the elimination of a small molecule, such as water, are called condensation reactions.

CONDENSATION REACTIONS

Reactions that involve the combination of two reactants and the elimination of a small molecule, such as water, are called **condensation reactions**. These reactions show the important role that functional groups of organic compounds play in the formation of larger biomolecules. When the functional groups on two separate molecules react, the two molecules are covalently bonded. This creates a structure that has the combined size of the two reactants. When this process continues, many molecules (monomers) can be joined like beads on a string, forming polymers.

FIGURE 9.3.11 The ripening of blackberries involves many chemical reactions, including the conversion of carboxylic acids to esters, giving a fruity, ripe odour.

Ester formation and hydrolysis

Many biomolecules are composed of esters. In the natural world, they give flowers and fruits their appealing aromas and tastes (Figure 9.3.11). For example, the ester 3-methylbutyl ethanoate gives bananas their aroma, and ethyl butanoate is found in pineapples.

Esters have the general structure shown in Figure 9.3.12.

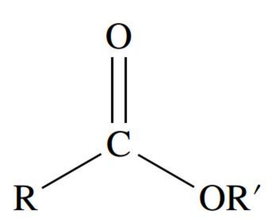


FIGURE 9.3.12 The general structure of esters

In this structure, we see a similarity to the carboxylic acids from which they are formed. The hydroxyl group (–OH) on the carboxylic acid has become an (–OR) group using the reaction described in Figure 9.3.13.

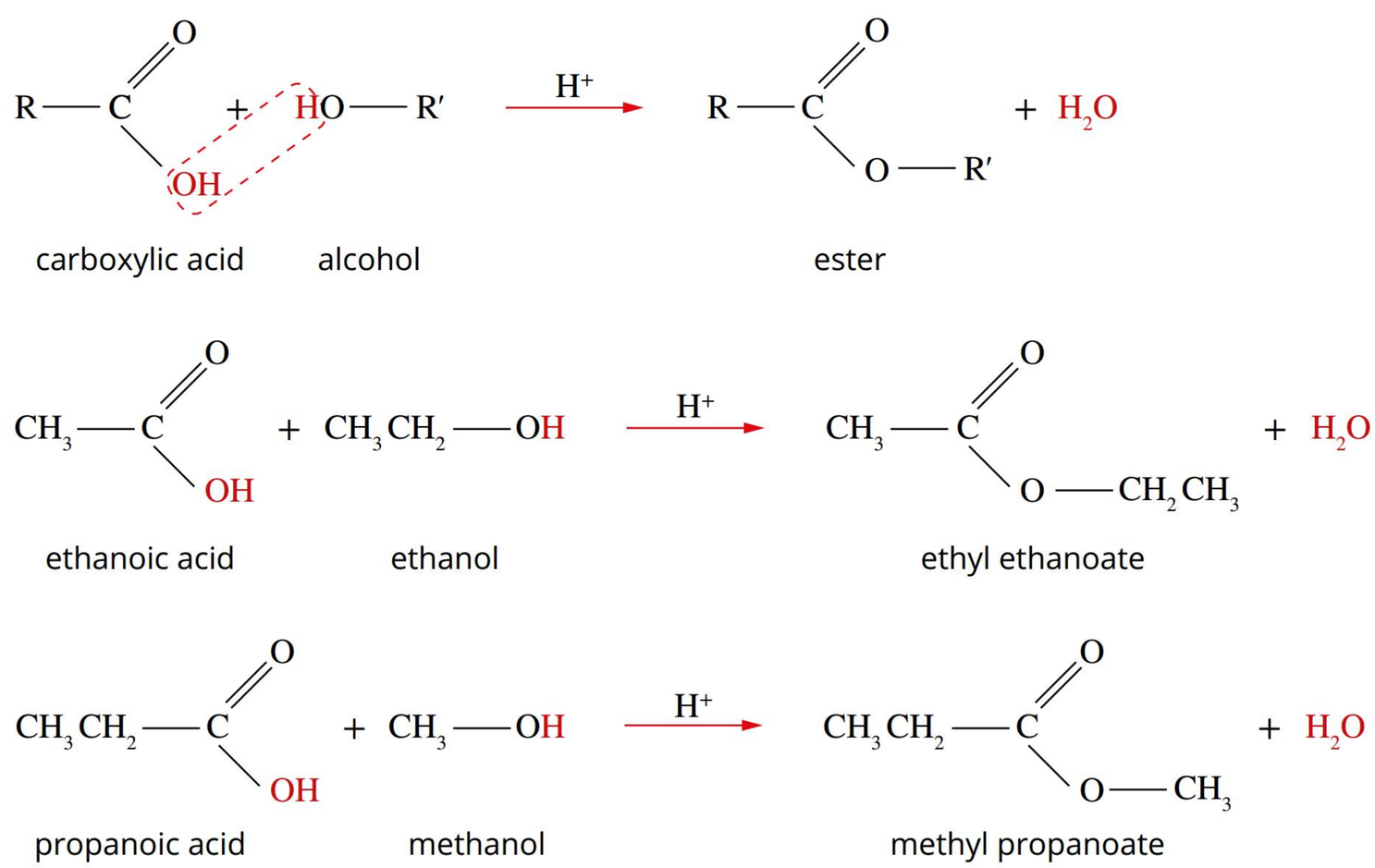


FIGURE 9.3.13 Esterification reactions occur when alcohols react with carboxylic acids and a small amount of sulfuric acid as a catalyst. The top reaction shows the general equation for esterification. Two specific examples are also shown: ethanoic acid with ethanol and propanoic acid with methanol.

Ester polymers (**polyesters**) are synthesised to provide a range of fabrics and plastic products. Fats and oils are **triglycerides**—ester molecules made from a combination of a glycerol molecule and three molecules of long-chain carboxylic acids called **fatty acids**. This can be seen in Figure 9.3.14. The condensation reaction is key to forming many natural and synthetic molecules and polymers.

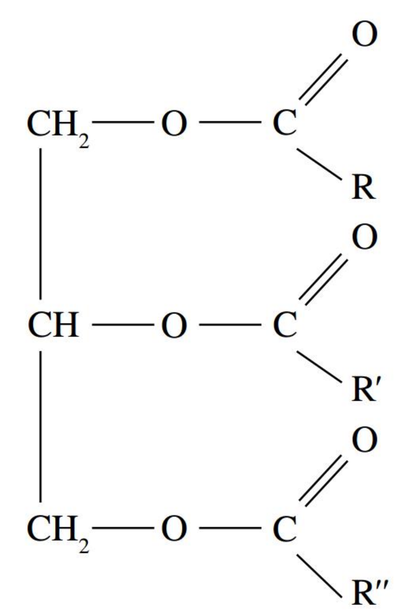


FIGURE 9.3.14 A triglyceride molecule showing its three long chains (R, R′, R″)

Esters are made by a condensation reaction between a carboxylic acid and an alcohol, also producing a water molecule. This is also known as an **esterification reaction**. For example, the ester ethyl ethanoate can be produced by reacting a mixture of ethanol and pure ethanoic acid with a trace amount of sulfuric acid. The sulfuric acid acts as a catalyst and the reaction will progress with little or no heating.

The general equation for the esterification reaction involving a carboxylic acid and an alcohol is shown in Figure 9.3.13. Two examples of esterification reactions are also shown.

In the esterification reaction, the hydrogen atom from the hydroxyl group of the alcohol and the –OH group from the carboxylic acid combine to form water, which is the molecule eliminated in this condensation reaction. This means that the alcohol becomes the alkyl group bonded to the oxygen in the final ester. We can see that, in the final ester, the part of the molecule derived from the carboxylic acid is identified by its C=O group, as shown in Figure 9.3.15.

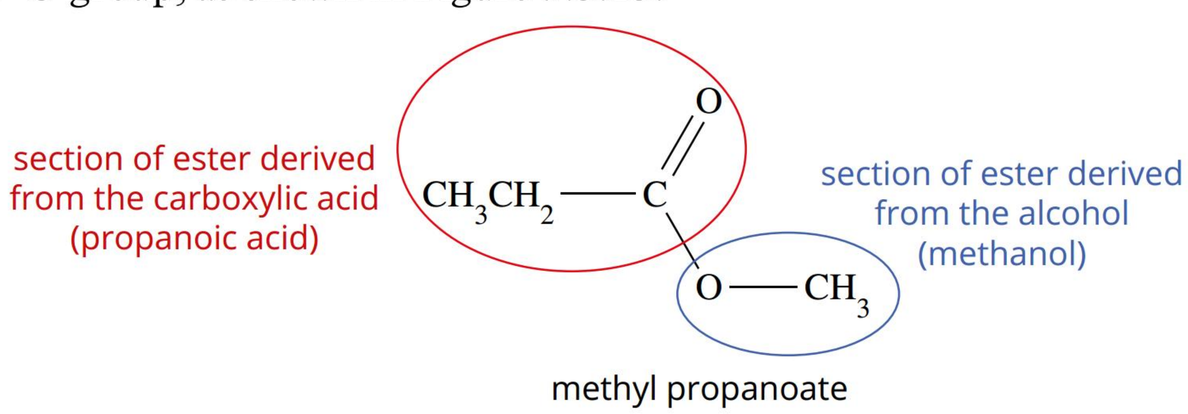
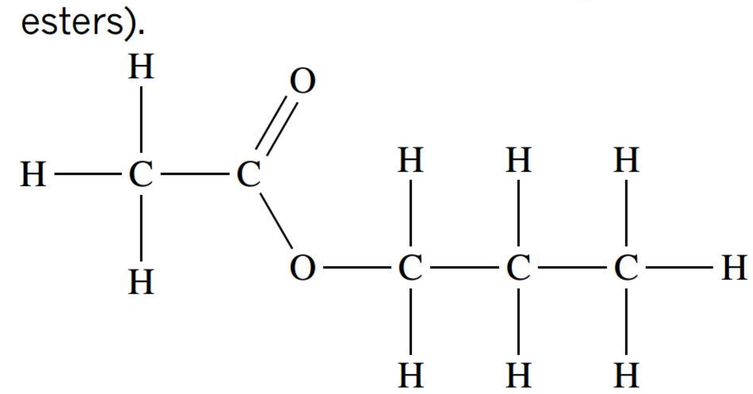


FIGURE 9.3.15 Identifying the acid and alcohol reacting to form an ester

As you learnt in Chapter 8, the first word of the name of an ester is derived from the name of the alcohol. The second word of the name is derived from the name of the carboxylic acid. Therefore, the name of the ester formed from methanol (alcohol) and propanoic acid (carboxylic acid) is methyl propanoate.

Worked example 9.3.2

DEDUCING THE PRODUCT OF AN ESTERIFICATION REACTION

Name and draw the product(s) of the reaction of propanol and ethanoic acid in the presence of a sulfuric acid catalyst.	
Thinking	**Working**
Use the organic reaction pathways in Figure 9.3.2 on page 371 to recall that a carboxylic acid and an alcohol will form an ester and water in the presence of an acid catalyst (condensation reaction).	An ester and a water molecule will be formed.
The first part of the name of the ester is derived from the name of the alcohol with '-yl' on the end.	propyl
The second part of the name is derived from the carboxylic acid with '-oate' on the end.	ethanoate
State the name using these two words.	propyl ethanoate
Recall that '-yl' refers to the part of the ester derived from the alcohol (propanol), and '-oate' refers to the part of the ester derived from the carboxylic acid (ethanoic acid). Draw an ester with two carbons in the part derived from the acid (contains a C=O), and three carbons in the part derived from the alcohol.	The ethanoate will have two carbons and the propyl will have three carbons. There will be COO in the centre (as for all esters). 

➤ Try yourself 9.3.2

DEDUCING THE PRODUCT OF AN ESTERIFICATION REACTION

Name and draw the product(s) of the reaction of butanol and pentanoic acid in the presence of a concentrated sulfuric acid catalyst.

The condensation reaction between carboxylic acids and alcohols is a reversible reaction. You can see in Figure 9.3.16 that esters can react with water to form a carboxylic acid and an alcohol. Reactions of this type are described as hydrolytic reactions, or simply **hydrolysis**. This reaction is catalysed by an alkali or dilute acid and requires heat to proceed. This means that an esterification reaction can be reversed by the addition of heat and dilute acid to the ester.

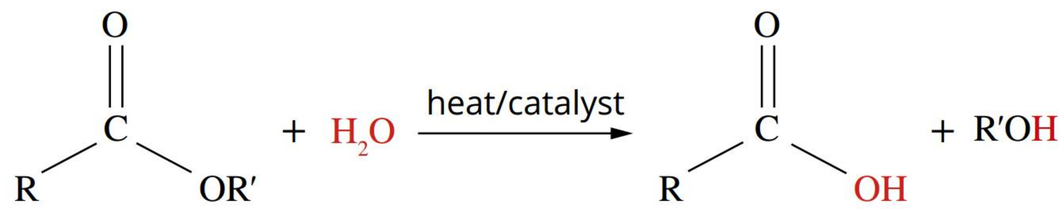


FIGURE 9.3.16 General equation for the hydrolysis of an ester

The products of a hydrolysis reaction can be deduced by identifying the carbon chain derived from the carboxylic acid and the carbon chain derived from the alcohol. Figure 9.3.17 shows the equation for the hydrolysis of ethyl propanoate to form ethanol and propanoic acid using an acid catalyst. In the ester, the chain

containing the C=O has three carbons and so we deduce that it was derived from propanoic acid. The chain on the other side of the oxygen atom has two carbons and so it must have been derived from ethanol. The products of hydrolysis of the ester, therefore, are propanoic acid and ethanol.

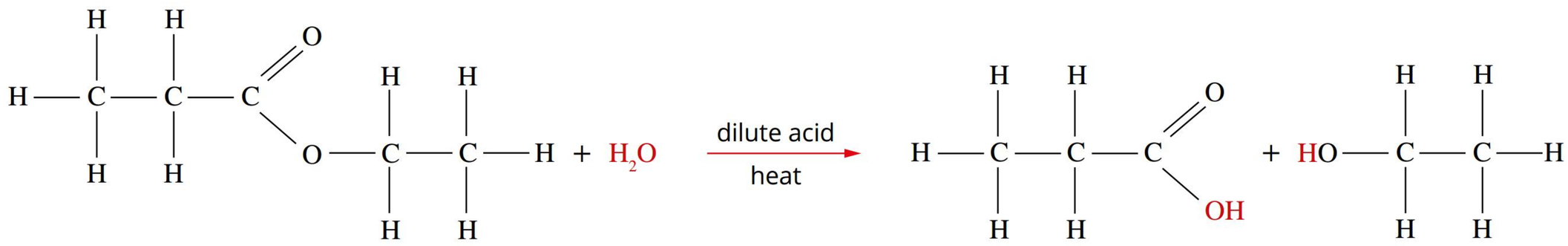
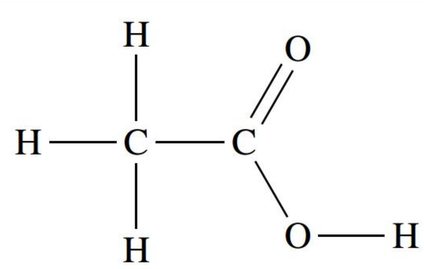
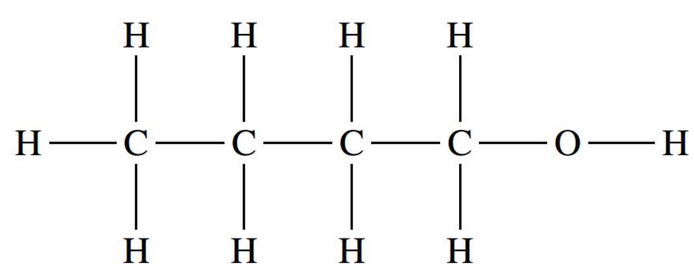


FIGURE 9.3.17 Equation for the acid-catalysed hydrolysis of ethyl propanoate to produce propanoic acid and ethanol

Worked example 9.3.3

DEDUCING THE PRODUCTS OF A HYDROLYSIS REACTION

Name and draw the products of the hydrolysis of the ester butyl ethanoate.	
Thinking	**Working**
Use the organic reaction pathways in Figure 9.3.2 on page 371 to recall that hydrolysis of an ester uses a water molecule and produces a carboxylic acid and an alcohol.	An acid molecule and an alcohol molecule will be formed.
Recall that in the name of the ester the '-yl' suffix indicates the carbon chain derived from the alcohol (butyl). This indicates the alcohol formed.	Butanol is formed.
Recall that in the name of the ester the '-oate' suffix indicates the carbon chain derived from the acid (ethanoic acid). This indicates the acid formed.	Ethanoic acid is formed.
OH is added to the two-carbon chain to form the acid. Draw the structure of ethanoic acid.	
H is added to the four-carbon chain to form the alcohol. Draw the structure of butanol.	

➤ Try yourself 9.3.3

DEDUCING THE PRODUCTS OF A HYDROLYSIS REACTION

Name and draw the products of the hydrolysis of the ester propyl methanoate.

Both ester formation (esterification) and ester hydrolysis are catalysed by acid. It may therefore seem impossible to identify the type of reaction and the reaction products occurring in the presence of acid. The key to this reasoning is the presence of water – it is a product of ester formation and a reactant in ester hydrolysis. By using concentrated acid (low water content), we promote esterification and by using

dilute acid (high water content), we promote the reverse reaction, hydrolysis. In this way, the presence of water affects the equilibrium position according to Le Chatelier principles.

Triglycerides from plant oils are esters that are hydrolysed using a special type of hydrolysis reaction called transesterification to produce biodiesel. The process is of great environmental importance as fossil fuels are replaced by sustainable and more carbon-neutral fuels. Refer to the Science as a Human Endeavour (SHE) article 'Biofuels from algae' for further recent developments in the production of biodiesel. One triglyceride molecule produces three biodiesel molecules in the following way (Figure 9.3.18):

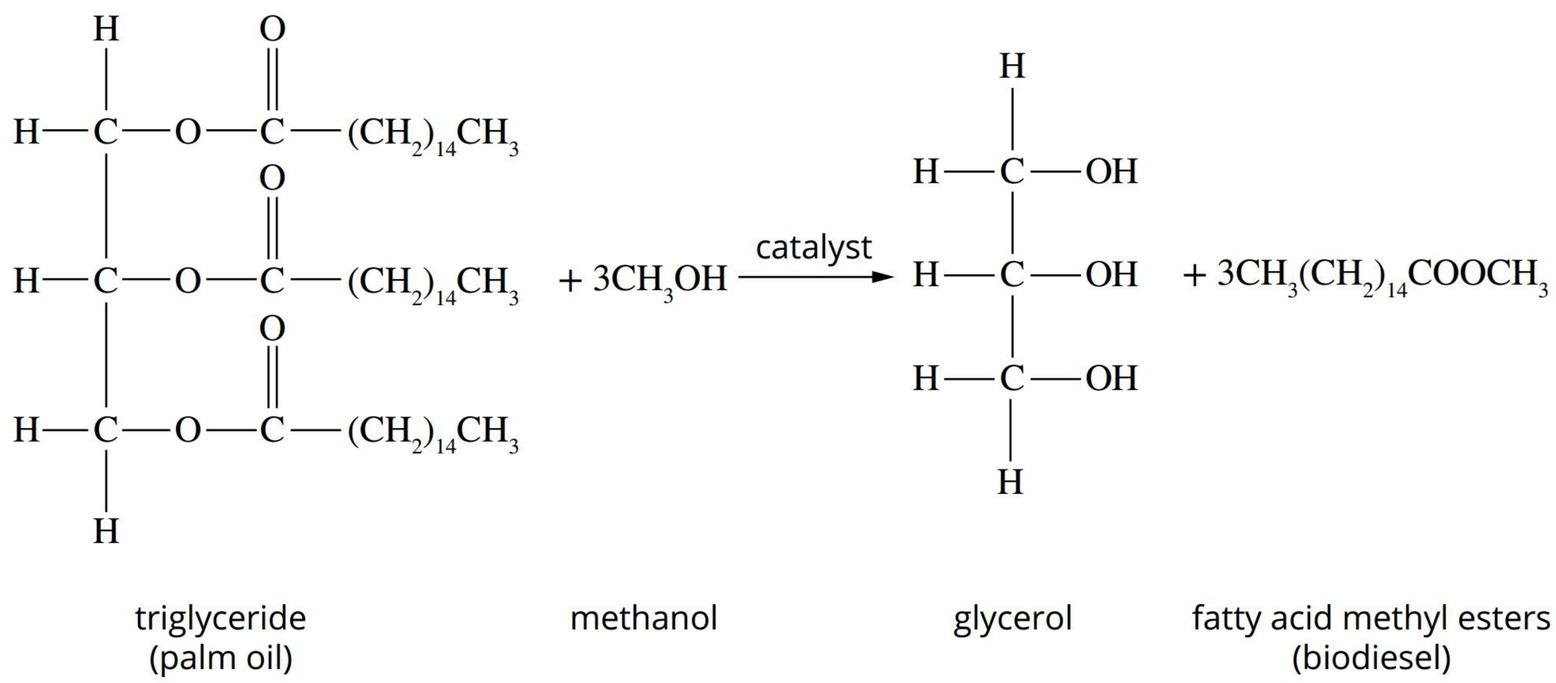


FIGURE 9.3.18 The reaction of a triglyceride with alcohol to form fatty acid esters (biodiesel)

Amide formation

Another key condensation reaction of carboxylic acids is the preparation of amides by the reaction of a carboxylic acid with ammonia or an amine. Primary amides ($RCONH_2$) can be prepared by the reaction of a carboxylic acid with ammonia. In Figure 9.3.19, you can see the production of ethanamide from ethanoic acid and ammonia. The reaction is a condensation reaction similar to the one you saw between a carboxylic acid and an alcohol to form an ester. A water molecule is produced during the reaction.

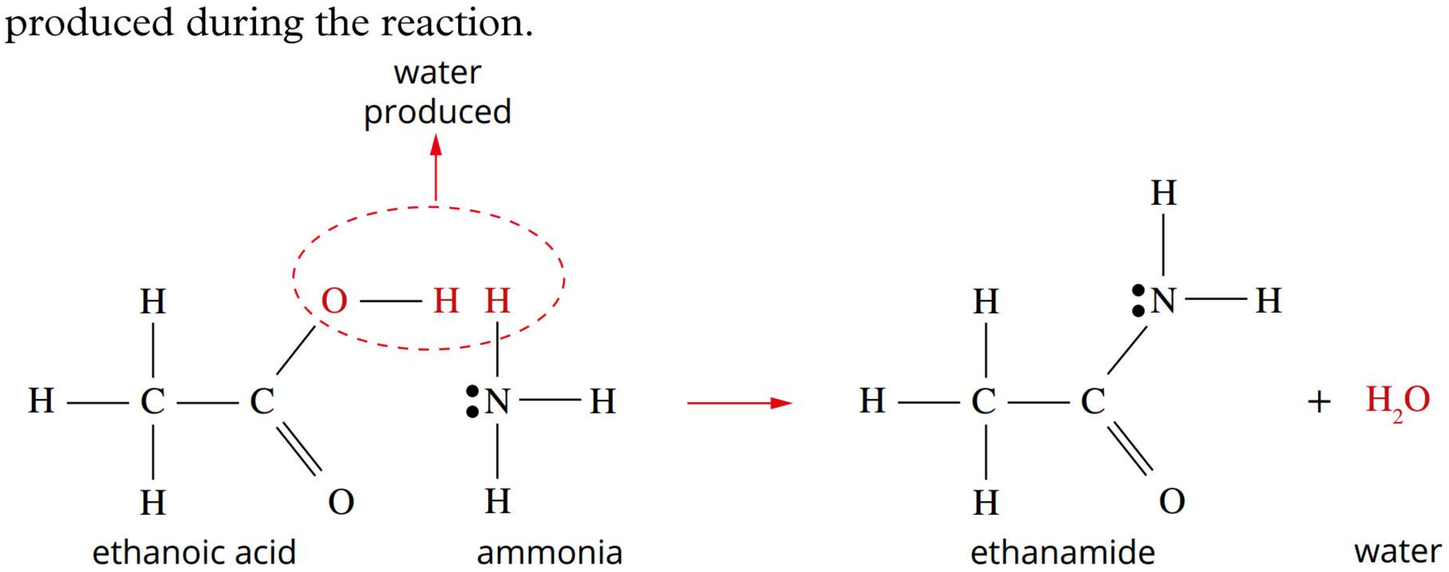


FIGURE 9.3.19 Reaction of ethanoic acid with ammonia to produce the primary amide ethanamide

Secondary amides have the general formula RCONHR′, where R and R′ represent alkyl groups. The condensation reaction between a carboxylic acid and an amine forms a secondary amide and a water molecule, as shown in Figure 9.3.20. An amide link is formed in this reaction.

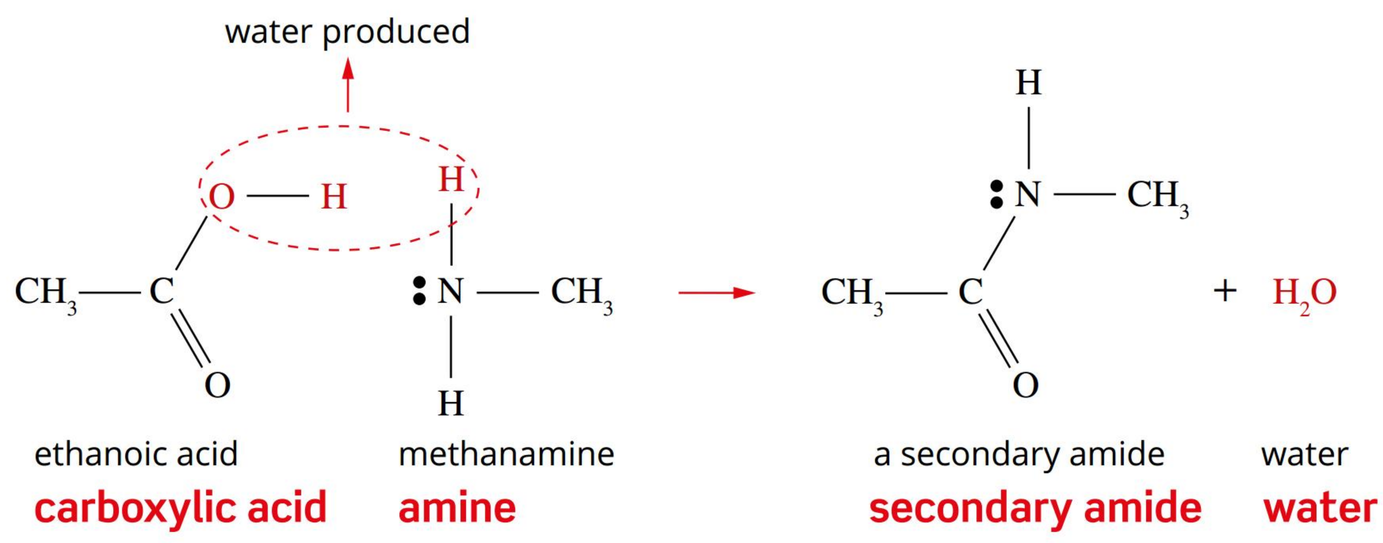


FIGURE 9.3.20 Formation of the secondary amide by a condensation reaction of ethanoic acid and an amine.

As described for esters, reaction conditions with low water (concentrated acid or base) will promote condensation (amide production) and reaction conditions with excess water present will promote hydrolysis of the amide.

Carboxylic acids undergo condensation reactions with alcohols to form esters, and with amines to form secondary amides.

9.3 Review

SUMMARY

- Alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides undergo reactions such as oxidation, reduction, condensation and hydrolysis.
- Alcohols undergo combustion when they react with oxygen to produce carbon dioxide, water and energy.
- Alcohols react with oxidising agents such as acidified solutions of dichromate ions and acidified permanganate ions in different ways.
  - Primary alcohols are oxidised first to aldehydes, which may be oxidised further to carboxylic acids.
  - Secondary alcohols are oxidised to ketones.
  - Tertiary alcohols are resistant to oxidation by these oxidising agents.
- Carboxylic acids react with alcohols in condensation reactions in the presence of a concentrated acid catalyst to produce esters.
- Esters can be hydrolysed by dilute acids to produce alcohols and carboxylic acids – the presence of water promotes the reaction.
- Carboxylic acids react with amines in a condensation reaction to form amides.
- The reactions can be represented by chemical equations using chemical formulas or structural formulas, with reaction conditions shown above the arrow.

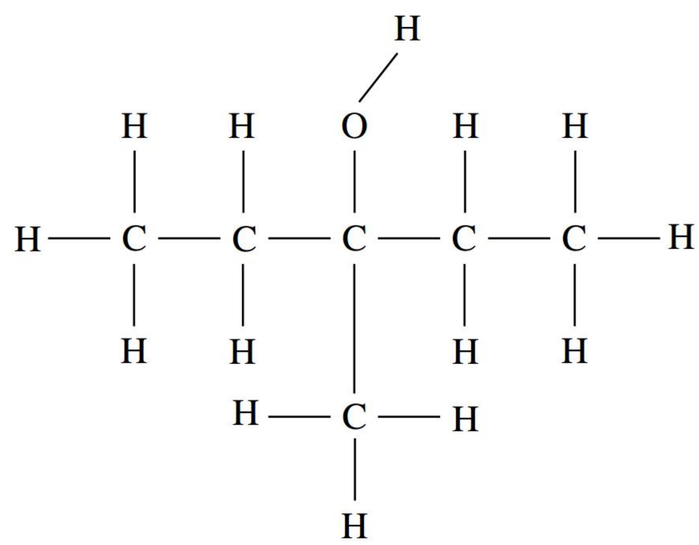
9.3 Review *continued*

KEY QUESTIONS

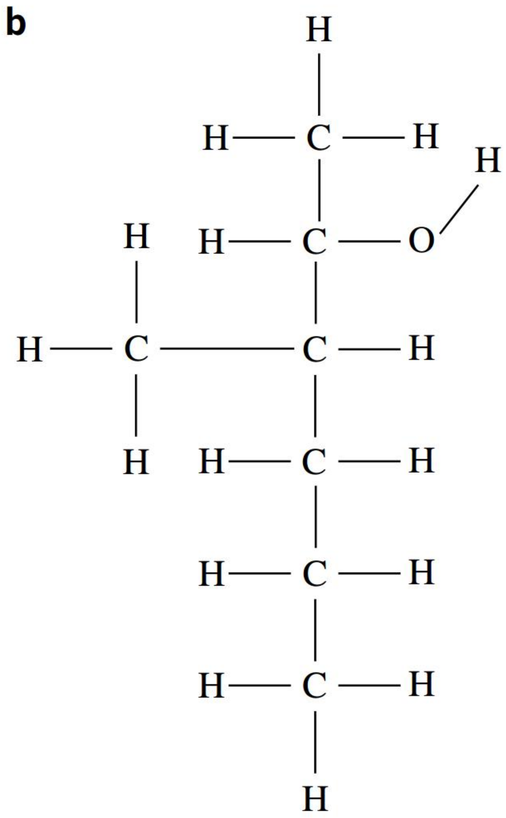
Describe

1 Identify each of the following alcohols as primary, secondary or tertiary.

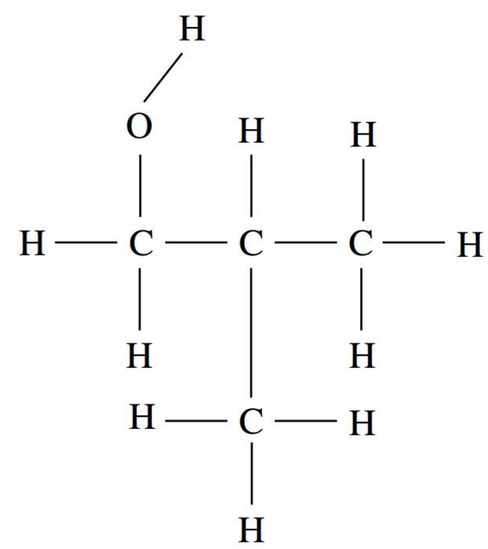
a



b



c



2 Pentan-3-ol, 2-methylbutan-2-ol and pentan-1-ol are all isomers of $C_5H_{12}O$.

- **a** Construct an equation for the complete combustion of $C_5H_{12}O$.
- **b** Identify each isomer as a primary, secondary or tertiary alcohol.
- **c** For each isomer, show the equation (using structural formulas) for the reactions that would occur if the alcohol was heated with acidified potassium permanganate solution. Describe any colour changes that would be observed.

3 Identify the products of a reaction in the following table where compounds A–D are heated with an acidified oxidising agent for an extended period of time.

Compound	IUPAC name	Product
A	butan-1-ol	
B	pentan-2-ol	
C	2-methylpentan-2-ol	
D	propan-2-ol	

4 **a** State what reaction conditions are required for the hydrolysis of an ester.

- **b** Name the products that would be formed from the acid hydrolysis of each of the following esters.
  - **i** $CH_3CH_2CH_2CH_2COOCH_3$
  - **ii** $CH_3COOCH_2CH_2CH_3$
  - **iii** $CH_3CH_2COOCH_2CH_2CH_2CH_2CH_2CH_3$

5 Recall the appropriate terms to complete the following sentences. When a carboxylic acid reacts with an amine, the organic product is an _____. The other product in this reaction is _____. This is an example of a _____ reaction.

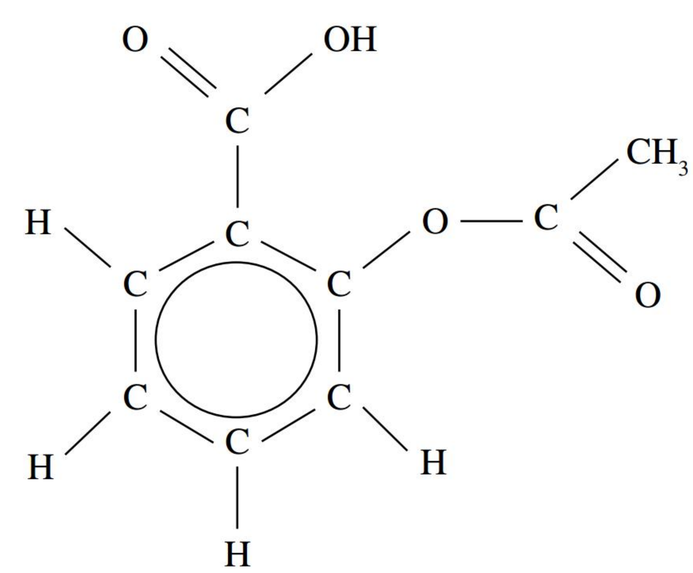
Apply

6 Draw and name the organic products of the reaction between:

- **a** methyl butanoate and dilute acid solution and heat
- **b** ethanol and propanoic acid, using concentrated sulfuric acid as a catalyst.

Analyse

7 The image below shows the chemical structure of aspirin (acetylsalicylic acid).



Identify the ester functional group in the structure of aspirin. Deduce the carboxylic acid that was used to prepare this ester.

9.4 Designing reaction pathways

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- recognise how organic chemistry reaction pathways are composed of individual reactions
- understand that reaction pathways may interconnect by having the same reactants and/or products
- distinguish reactions that require special conditions or catalysts to proceed
- deduce reaction pathways given a reactant and/or product
- understand conditions and catalysts necessary for certain reactions.

Organic chemists focus on developing compounds that have exactly the right properties needed for a particular purpose. These may be new pharmaceuticals, polymers or nanomaterials. Once the desired compound has been identified, chemists must devise a way to make it. This means devising an efficient method for converting readily available starting materials—often alkenes or alkanes—into the more complex product(s) required.

In this module, you will learn how to devise reaction pathways for the synthesis of some simple organic compounds by utilising the reactions you have learnt about in Modules 9.2 and 9.3. This module will use both short and longer synthetic pathways to demonstrate and test your understanding and knowledge of the reactions.

REACTION PATHWAYS FOR ORGANIC COMPOUNDS

The in-depth discussions of organic chemistry reaction pathways provided in Modules 9.2 and 9.3 have focused on six key types of chemical reactions:

- oxidation
- reduction
- addition
- condensation and hydrolysis
- elimination
- substitution.

These chemical reactions are summarised in Figure 9.4.1. You have learnt that simpler molecules such as alkanes, alkenes and alcohols may be used as starting materials to make other molecules such as carboxylic acids, esters and amides. This means that they are precursors of the final product, or target molecules. The individual reactions are a series of steps or stages that make up a reaction pathway that can be used to convert a reactant containing certain functional groups to a desired product with different functional groups.

For example, Figure 9.4.1 shows that an alcohol can be produced by starting with a haloalkane, enacting an elimination reaction to produce an alkene, or formed directly through a substitution reaction between the haloalkane and sodium hydroxide. The choice of reaction depends on the nature of the alcohol required. Both the haloalkane and the alkene are precursors of the alcohol. The elimination reaction removes a hydrogen halide, and the addition reaction adds a water molecule. Note also that if the haloalkane was not available for this pathway, it could be synthesised using a substitution reaction with an alkane.

You have also learnt that inorganic reactants are required for these reactions and that some of these reactions require special conditions to proceed (Figure 9.4.2).

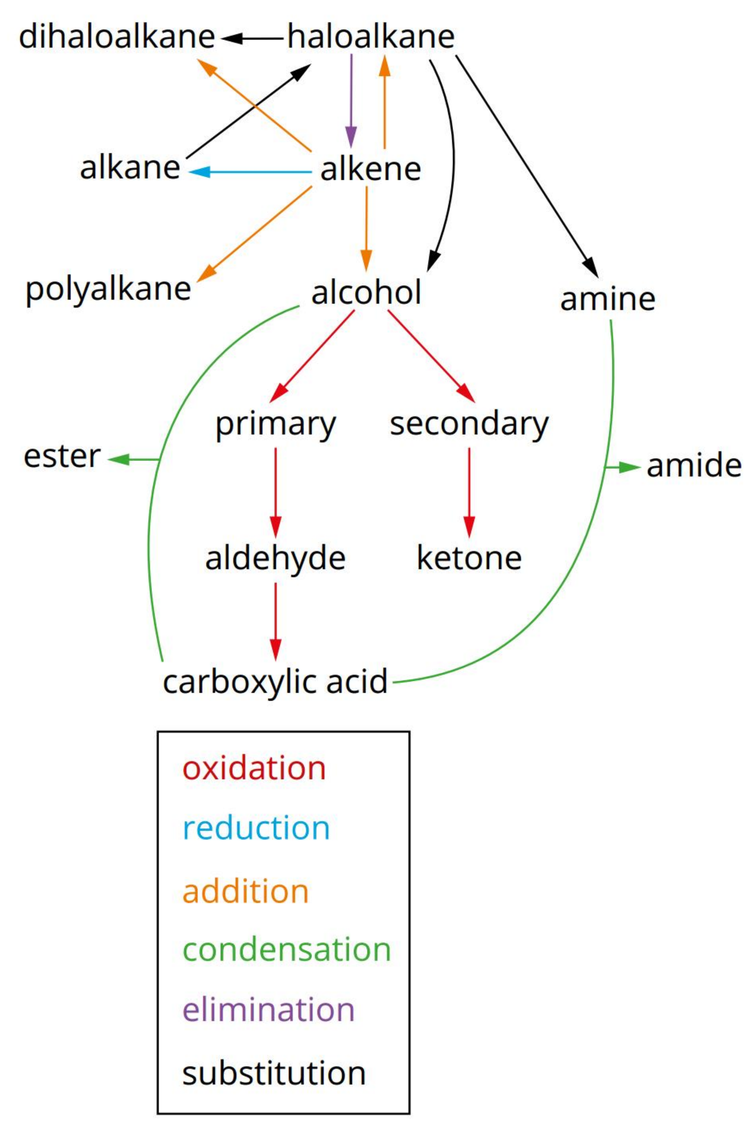


FIGURE 9.4.1 Common organic chemical pathways

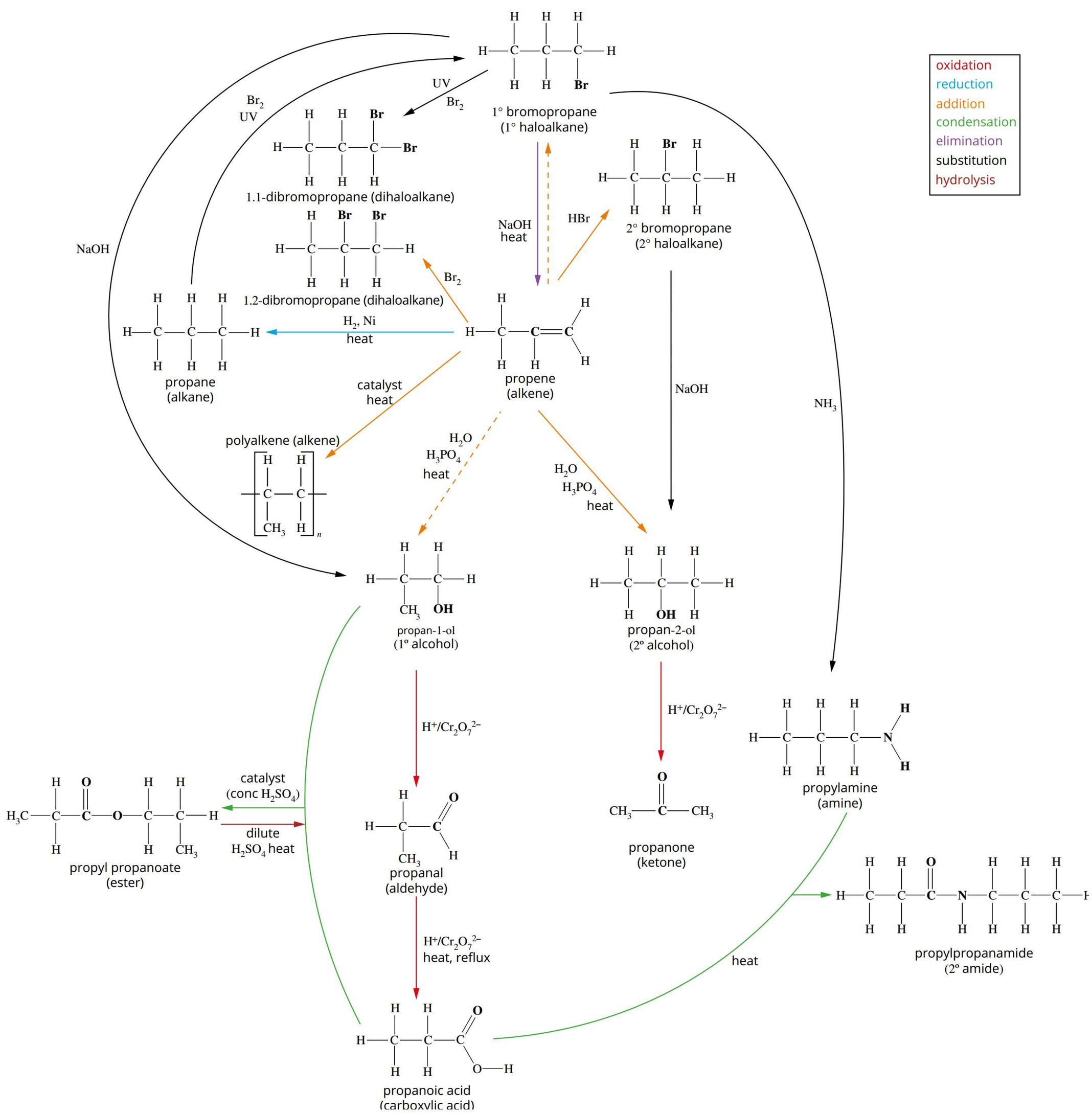


FIGURE 9.4.2 Reaction pathways described in this chapter showing chemical structures and reaction conditions such as catalysts (metal or acid), heat or oxidising agent (e.g. $H^+/Cr_2O_7^{2-}$). Functional groups are shown in bold. Note that addition reactions of alkenes must follow Markovnikov's rule and therefore the major product of H_2O addition to an alkene is a secondary alcohol, not primary alcohol. A small amount of the primary alcohol is produced (dashed arrow). Similarly, the addition reaction producing 2° bromopropane from propene will have a major and minor product according to Markovnikov's rule.

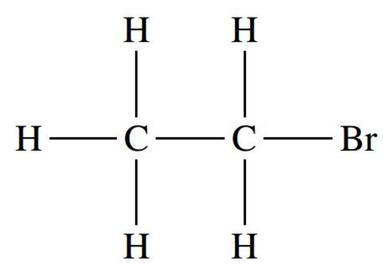
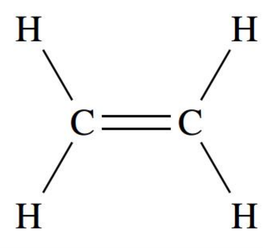
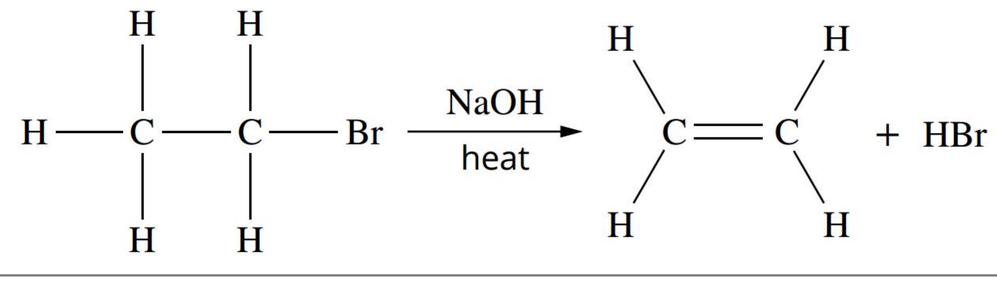
These conditions include catalysts (such as metal or acid), heat or an acidified oxidising agent (e.g. $H^+/Cr_2O_7^{2-}$). You will notice that the structural formulas shown in Figure 9.4.2 give a better visual understanding of the chemical changes because functional groups (shown in bold) are clearly visible in each structure.

By understanding and recalling the reactions shown in Figure 9.4.2, you should be able to deduce the organic product from given starting molecules and reaction type. Conversely, the precursor can be deduced using information given

about the product and process. For example, synthesis of ethanol can occur in two ways. Firstly, a substitution reaction of chloroethane with NaOH could be used. Alternatively, an addition reaction of water and propene using heat and dilute acid catalyst. The following shows a simple and then a more complex deduction using the pathways in Figure 9.4.2.

Worked example 9.4.1

DEDUCING A SIMPLE REACTION PATHWAY

Use structural formulas to show the chemical reaction by which ethene is synthesised by an elimination reaction.	
Thinking	**Working**
Use the reaction pathways in Figure 9.4.2 on page 384 to recall that alkenes are made from haloalkanes by an elimination reaction. The haloalkane required must have two carbon atoms.	
Recall that NaOH is required for this reaction to proceed and heat must be used because milder reaction conditions will favour substitution. NaOH is a catalyst not a reactant, and so is written above the arrow in the chemical equation.	NaOH, heat
The reaction eliminates HBr, allowing a double bond to form between the two carbon atoms.	
	

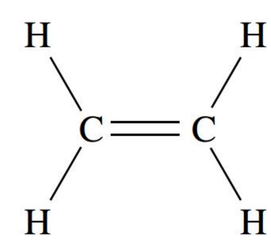
➤ Try yourself 9.4.1

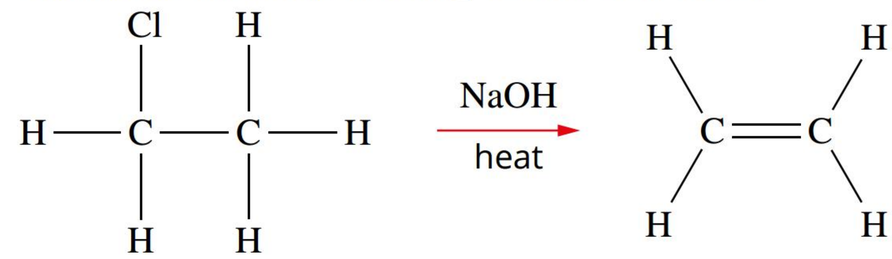
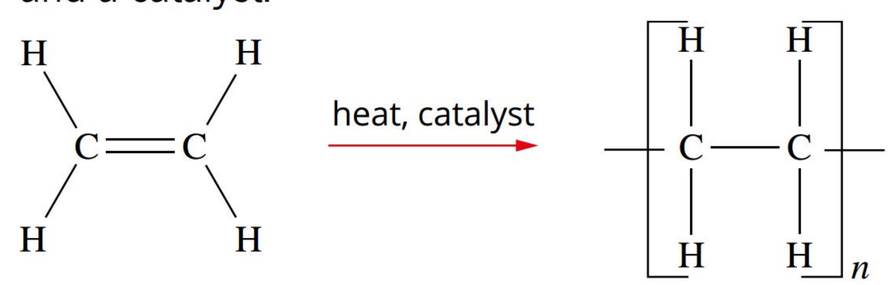
DEDUCING A SIMPLE REACTION PATHWAY

Use structural formulas to show the chemical reaction by which 1-chloropropane is synthesised by a substitution reaction.

Worked example 9.4.2

DEDUCING A COMPLEX REACTION PATHWAY

Describe the reaction(s) required to synthesise polyethene from chloroethane. Draw all relevant structures.	
Thinking	**Working**
Use the organic reaction pathways in Figure 9.4.2 on page 384 to recall that polyalkenes are synthesised from alkenes. The pathway required is: haloalkane → alkene → polyalkene	Synthesis of polyethene requires first making ethene. 

The reactant provided (chloroethane) must be converted to an ethene first. Sodium hydroxide (NaOH) and heat must be used for the elimination reaction. Milder conditions will favour the substitution reaction.	To make ethene, chloroethane undergoes an elimination reaction using NaOH and heat. 
A second reaction is required. This is the synthesis of polyethene from the ethene.	Then ethene is converted to polyethene using heat and a catalyst. 

➤ Try yourself 9.4.2

DEDUCING A COMPLEX REACTION PATHWAY

Describe the reaction(s) required to synthesise ethanoic acid from ethene. Draw all relevant structures.

In Chapter 8, you learnt about reaction pathways using condensed structural formulas. The following chemical equation shows condensed structural formulas for the reaction shown in Worked example 9.4.1:

$$CH_3CH_2Br \xrightarrow{\text{UV light}} CH_2CH_2 + HBr$$

Condensed structural formulas are often a more efficient way to depict complex organic chemistry pathways than using structural formulas. Figure 9.4.3 shows a five-step reaction pathway, where an ester has been synthesised from an alkane (ethane). In this reaction pathway, we see that the target molecule, an ester, has five precursors and is the result of five chemical reactions. It is clear that condensed structural formulas provide an efficient notation in these situations.

$$CH_3CH_3 + Cl_2 \xrightarrow{\text{UV light}} CH_3CH_2Cl \xrightarrow[\text{heat}]{\text{NaOH}} CH_2CH_2 \xrightarrow[\text{heat}]{H_2O,\ H_3PO_4} CH_3CH_2OH \xrightarrow[\text{heat, reflux}]{H^+/Cr_2O_7^{2-}} CH_3COOH + ROH \xrightarrow{\text{conc } H_2SO_4} CH_3COOR + H_2O$$

FIGURE 9.4.3 Reaction pathway showing the synthesis of an ester from an alkane

Considerations in reaction pathways

To produce a target molecule, there must be sufficient quantities of all reactants. In addition, you have learnt that organic chemistry pathways often require catalysts and specific conditions for reactions to proceed. The role of these conditions and catalysts is to promote interactions between reacting molecules. They have the effect of enhancing charge interactions between molecules, as described in Module 9.1. Pathways diagrams do not show balanced equations. The organic component is shown, and other reactants and reaction conditions are shown above or below the arrow. Reactants and conditions that we have learnt about in our study of organic reactions are heat, metal catalysts, oxidising agents, strong acids or strong bases, as shown in Figure 9.4.2 on page 384. They are written above or below the arrow in a chemical equation and either catalyse/promote the reaction or take part in it.

When water is a reactant or product the reaction can usually be reversed by its presence. For example, both the alkene → alcohol reaction and the alcohol/acid → ester reaction are catalysed by acid. Water is a reactant. To promote alkene → alcohol reaction, use dilute acid because water is required as a reactant. To reverse the reaction, use concentrated acid or use an acid/alcohol mix which has no water

present. Similarly, the hydrolysis of an ester uses water, so use dilute acid – to produce an ester (the reverse reaction), use a concentrated acid or acid/alcohol mix.

Often combinations of reaction conditions are used, and more than one reagent will achieve the result. For example, the oxidising agent acidified MnO_4^- can be substituted for acidified $Cr_2O_7^{2-}$. Metal catalysts can include Pt, Pd, as well as Ni. Also, H_3PO_4 may be substituted for the acid catalyst H_2SO_4.

By writing some general rules, these conditions can be more easily recalled. Table 9.4.1 summarises reaction type and conditions used. Most but not all reactions learnt in this chapter are represented here, and some of these reactions also require the application of heat.

TABLE 9.4.1 Some general rules for organic reaction conditions

Reaction type	Conditions used
oxidation	MnO_4^- or $Cr_2O_7^{2-}$ in acidic solution*
reduction	Ni, Pd or Pt (metal catalyst), heat
elimination	NaOH, heat

*to oxidise an aldehyde to a carboxylic acid, heat/reflux must also be used

USING REACTION PATHWAYS

The complex understanding of interconversion of organic compounds that you have developed in this chapter means that you can devise laboratory procedures to produce a required compound. These procedures may have one or several reactions or steps comprising the overall reaction pathway. Reaction pathways can be compared to travelling in a car. Origin, destination and route must be considered. Using this analogy, we can compare Figures 9.4.1 and 9.4.2 to a map that indicates possible routes on which to travel to reach a destination. While you are expected to be familiar with the reactions described here, explanation of pathways with multiple steps (more than two) is not required.

Making ethyl ethanoate

Suppose you wanted to form ethyl ethanoate using only alkenes as starting materials. A close look at the structure of the compound shown in Figure 9.4.4 will show you that it is an ester produced by the condensation reaction between ethanoic acid and ethanol. We know this because the structure shows two different alkyl or R groups, with an ester functional group in the middle. The group containing C=O is derived from the carboxylic acid, and the group containing the –O is derived from the alcohol. This information is also obtained from the name of the ester. The 'yl' suffix indicates the alcohol (ethanol) that reacted to produce the ester, and the 'oate' suffix indicates the reacting carboxylic acid (ethanoic acid) that reacted to produce the ester.

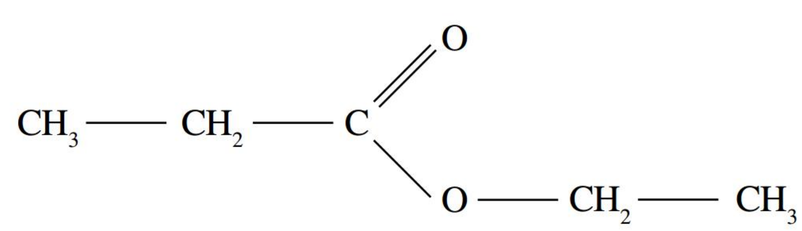


FIGURE 9.4.4 Structure of ethyl ethanoate

To form ethyl ethanoate, ethanol and ethanoic acid need to be synthesised first, before they can react to form the ester. As described, the designated reactants are alkenes. This means that the strategy to form ethyl ethanoate is to use an alkene to make ethanol and ethanoic acid, followed by a reaction of these two to form the ester.

Reagents and conditions for making ethanol

Ethanol can be synthesised from ethene by the addition reaction with water, as shown in Figure 9.4.5. You can see the conditions for the reaction require an acid catalyst (placed above the arrow) and a reactant (H_2O).

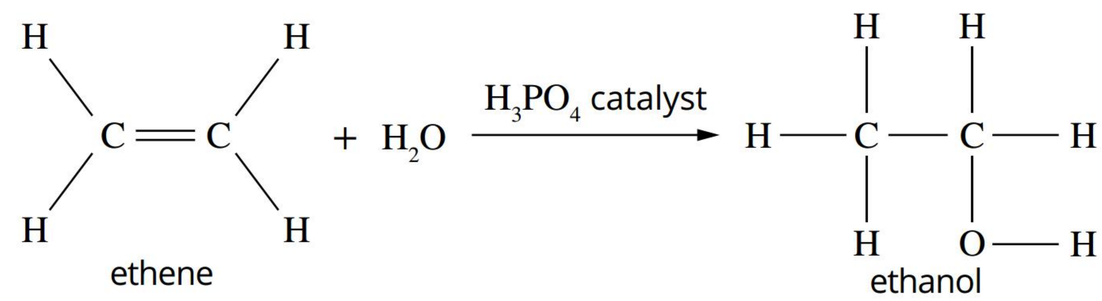


FIGURE 9.4.5 Synthesis of ethanol using ethene

Reagents and conditions for making ethanoic acid

Ethanoic acid is a carboxylic acid containing two carbon atoms. It can be prepared by the pathway shown in Figure 9.4.6. If you work backwards from ethanoic acid, you can see that it can be formed from the oxidation of the primary alcohol ethanol. This in turn can be formed by the reaction of ethene with water in the presence of phosphoric acid catalyst.

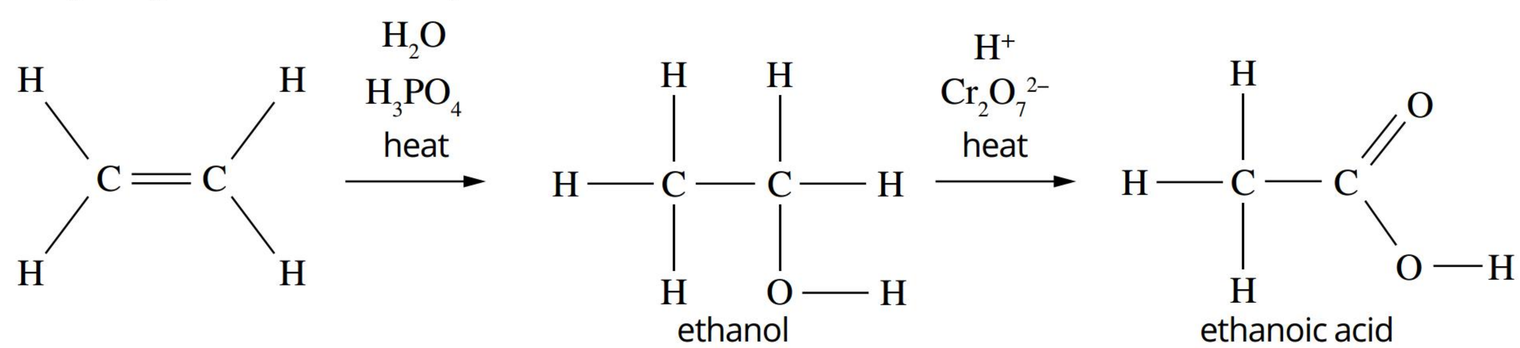


FIGURE 9.4.6 Synthesis of ethanoic acid from ethene

As this is a reaction pathway (as opposed to a balanced equation), both the other reactant and any reaction conditions are shown above the arrow. Having synthesised ethanol and ethanoic acid, you can now prepare the ester, ethyl ethanoate, using a condensation reaction, as shown in Figure 9.4.7.

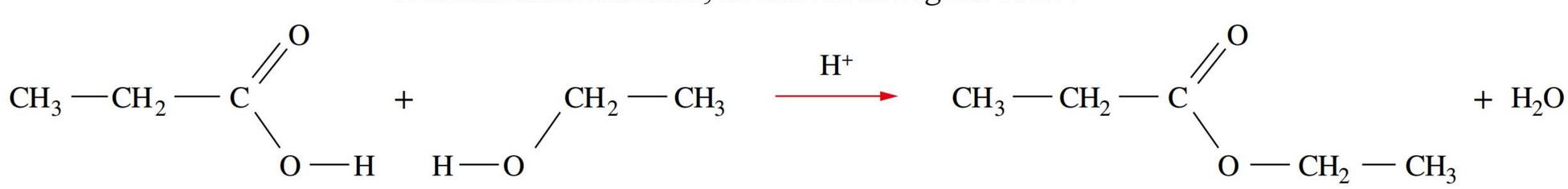


FIGURE 9.4.7 The formation of ethyl ethanoate from the condensation reaction of ethanol and ethanoic acid

The full reaction pathway for the preparation of ethyl ethanoate from ethene via ethanol and ethanoic acid is summarised in Figure 9.4.8.

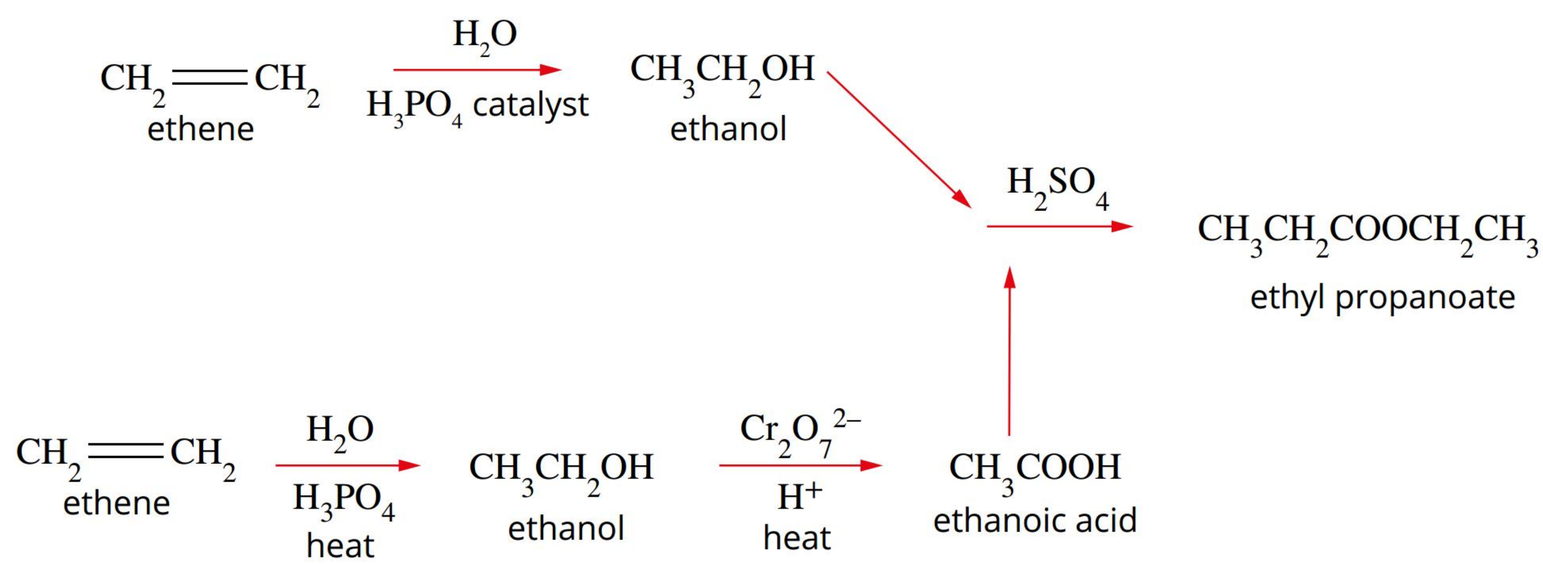
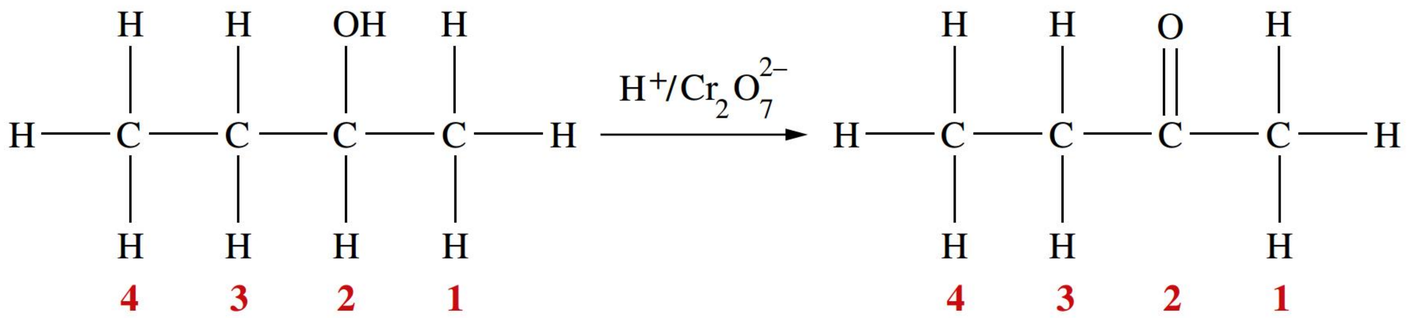
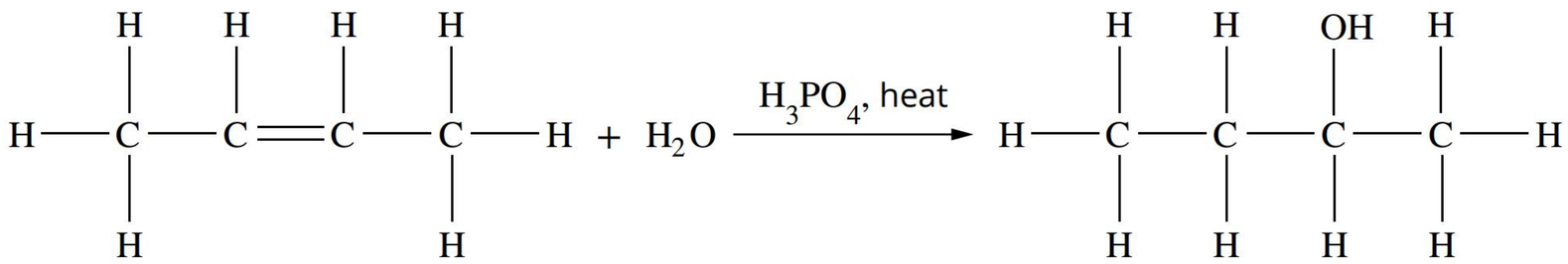


FIGURE 9.4.8 Reaction pathway for the preparation of ethyl ethanoate from ethene

A reaction pathway summarises the reactions required to produce a product from simple starting materials.

Worked example 9.4.3

DEDUCING A REACTION PATHWAY

Describe the reaction pathway for the synthesis of butan-2-one from but-2-ene.	
Thinking	**Working**
Use the organic reaction pathways in Figure 9.4.2 on page 384 to work backwards and recall that butan-2-one is synthesised from butan-2-ol by an oxidation reaction with dichromate ions in an acidic solution.	The second reaction of the pathway produces butan-2-one by an oxidation reaction of butan-2-ol with dichromate ions in an acidic solution. 
Work backwards to but-2-ene from butan-2-ol (secondary alcohol). The reaction that produces the alcohol from the alkene requires water as the other reactant, phosphoric acid and heat.	The first reaction of the pathway produces butan-2-ol by an addition reaction of but-2-ene with phosphoric acid. 
Show the reaction pathway in order of progression.	$CH_3CHCHCH_3 + H_2O \xrightarrow{H_3PO_4, heat} CH_3CH_2CHOHCH_3 \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3CH_2COCH_3$

The addition of water to but-1-ene would mostly yield butan-2-ol, with Markovnikov's rule adding the H to carbon number 1 and the OH to carbon number 2. Therefore, it is important when designing reaction pathways to consider different options. This will be covered in Module 12.1 through a discussion of retrosynthetic pathways and atom economy (Module 12.8).

➤ Try yourself 9.4.3

DEDUCING A REACTION PATHWAY

Describe the reaction pathway for the synthesis of propan-1-amine (propylamine) from propane.

The flow chart in Figure 9.4.9 shows some of the stages in the planning process for a synthesis scheme.

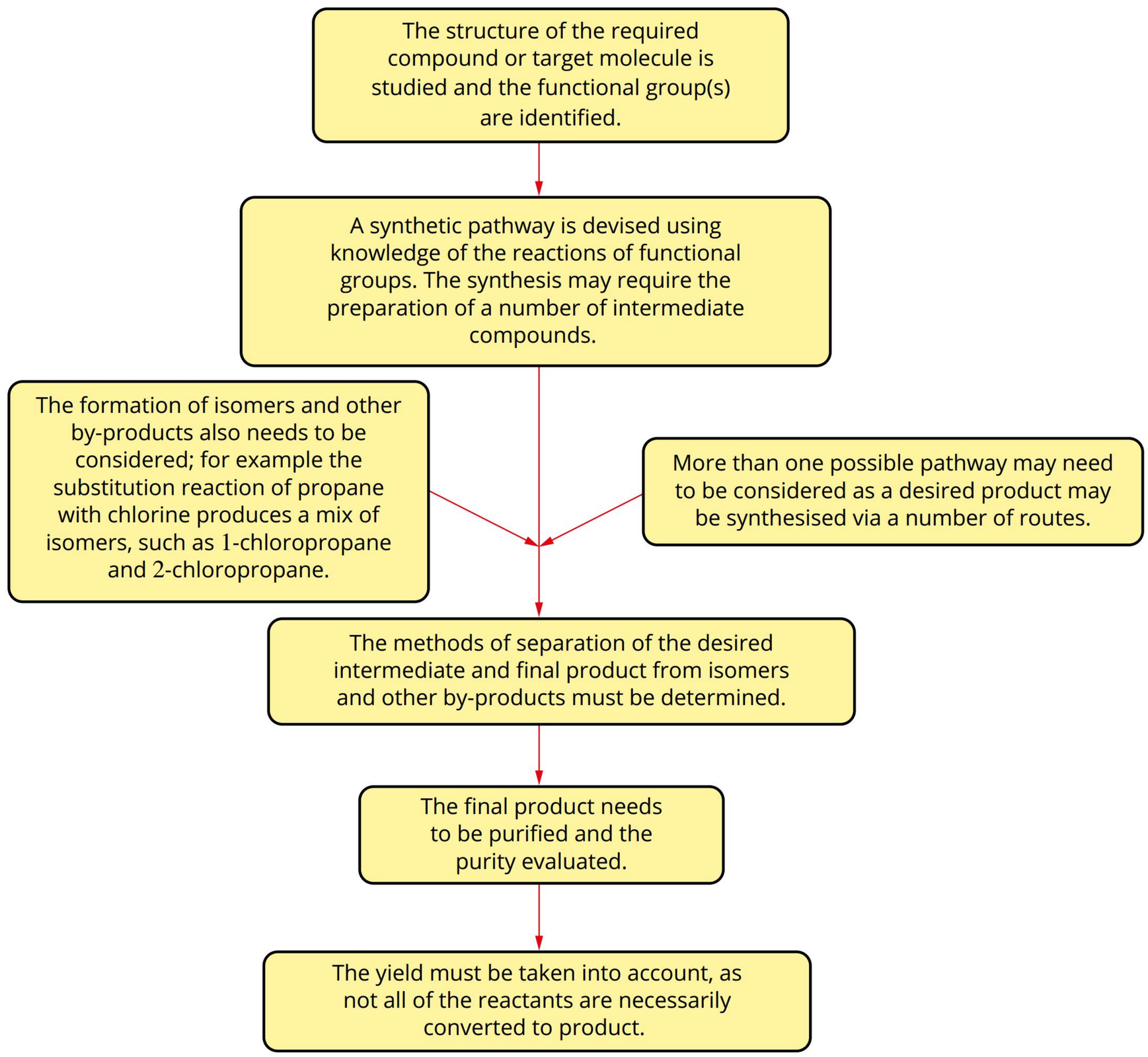


FIGURE 9.4.9 Steps in the design of a synthetic pathway of an organic compound

9.4 Review

SUMMARY

- A reaction pathway is a sequence of more than one reaction that is used to convert a reactant into a product.
- Reaction pathways can be constructed using the organic reactions studied in this chapter.
- Reaction pathways indicate the reaction conditions and reagents required for each step.

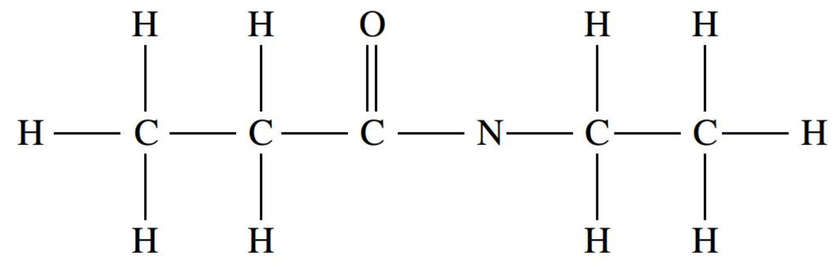
KEY QUESTIONS

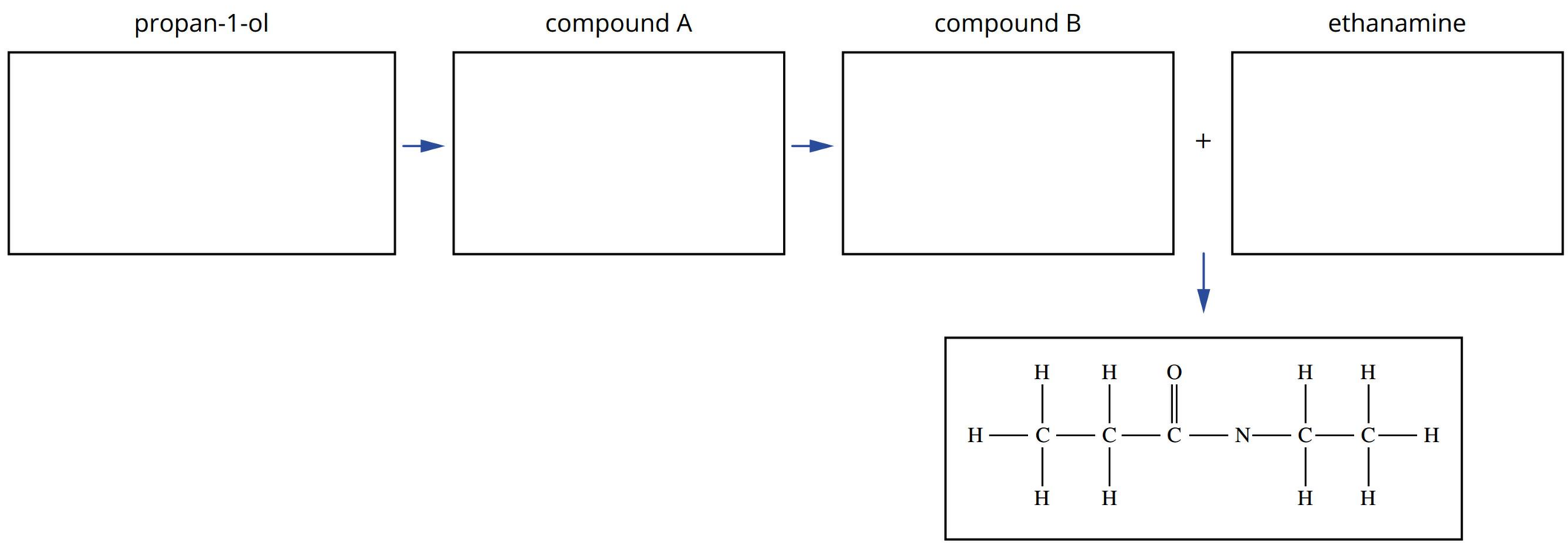
Describe

1 Identify which of the following is involved in an addition reaction when an alcohol is formed from an alkene.

A a metal catalyst
B sodium hydroxide
C steam and an acid catalyst
D reaction with a halogen gas

2 N-ethylpropanamide (shown below) can be made using the pathway outlined by the partially completed scheme below.





a Identify compound A by drawing the structural formula in the pathway diagram.

b Name the chemical used to convert propan-1-ol to compound A.

c Identify compound B by drawing the structural formula in the pathway diagram.

d Name the chemicals and the reaction conditions used to convert compound A to compound B.

e State the name of the final reaction and the inorganic product.

Apply

3 Show reaction pathways for the following reactions.

a ethanamine from chloroethane

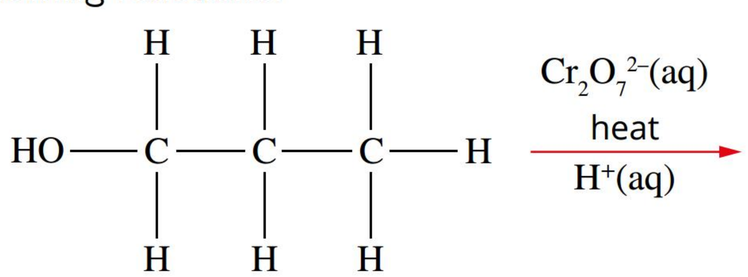
b butan-1-ol from butane

c pentanoic acid from 1-chloropentane

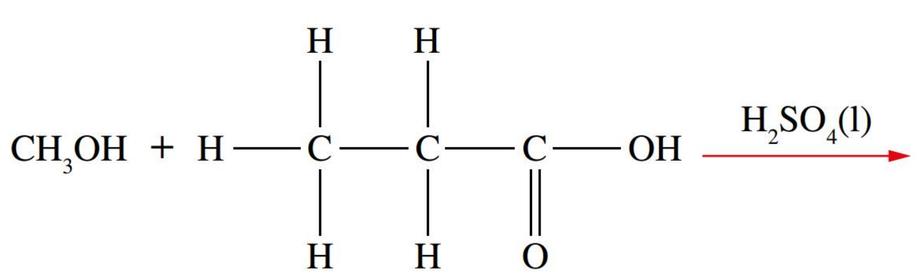
4 Describe a reaction pathway to synthesise butyl ethanoate from the appropriate butane and ethene starting materials.

5 Draw the structural formulas of the products of the following reactions.

a



b



Analyse

6 A student reacted a sample of bromopropane with ammonia, and then reacted the product with butanoic acid.

a Determine the names of the two reactions occurring.

b Deduce the class and the structural formula of the final product.

7 A sample was reacted with chlorine gas under UV light, then the substance was reacted with sodium hydroxide and heat. The final product was shown to change bromine water from brownish-red to colourless. Deduce which of the following correctly lists the likely changes to the contents of the test tube.

A alkene $\xrightarrow{\text{addition}}$ haloalkane $\xrightarrow{\text{elimination}}$ alkene

B alkane $\xrightarrow{\text{substitution}}$ haloalkane $\xrightarrow{\text{addition}}$ alkene

C alkene $\xrightarrow{\text{reduction}}$ alkane $\xrightarrow{\text{substitution}}$ haloalkane

D alkane $\xrightarrow{\text{substitution}}$ haloalkane $\xrightarrow{\text{elimination}}$ alkene

8 Describe the reason that producing a carboxylic acid from ethene is much simpler than producing a carboxylic acid from propene or butene.

9 Compare the reaction between a carboxylic acid and an amine to an inorganic neutralisation reaction (e.g. HCl and NaOH).

Chapter review

09

KEY TERMS

addition polymerisation
addition reaction
alkyl group
catalyst
combustion
complete combustion
condensation reaction
elimination reaction
esterification reaction
exothermic
fatty acid
fractional distillation
hydrolysis
Markovnikov's rule
monomer
oxidation–reduction reaction
polar bond
polyester
polymer
reaction pathway
substitution reaction
triglyceride
reflux

KEY QUESTIONS

Describe

1 When an ester is formed from a carboxylic acid and an alcohol, the condensation reaction that occurs involves:

A two hydroxyl functional groups
B a carboxyl functional group and an amino functional group
C a hydroxyl functional group and a carboxyl functional group
D a hydroxyl functional group and an amino functional group.

2 Substances that are required to make organic reaction pathways proceed but are not used up in the reaction are called:

A catalysts
B products
C reactants
D precursors.

Questions 3–6 refer to the following information.

The following list gives the formulas of a number of organic molecules.

I CH_3CH_2COOH
II $CH_3CH_2CH_2CH_2NH_2$
III CH_3OH
IV $CH_2CHBrCH_3$
V $CH_3CH_2CH_2CH_3$
VI $CH_3CHCHCH_3$

3 Identify two molecules that would react together to form an ester.

A I and III
B I and V
C III and IV
D IV and VI

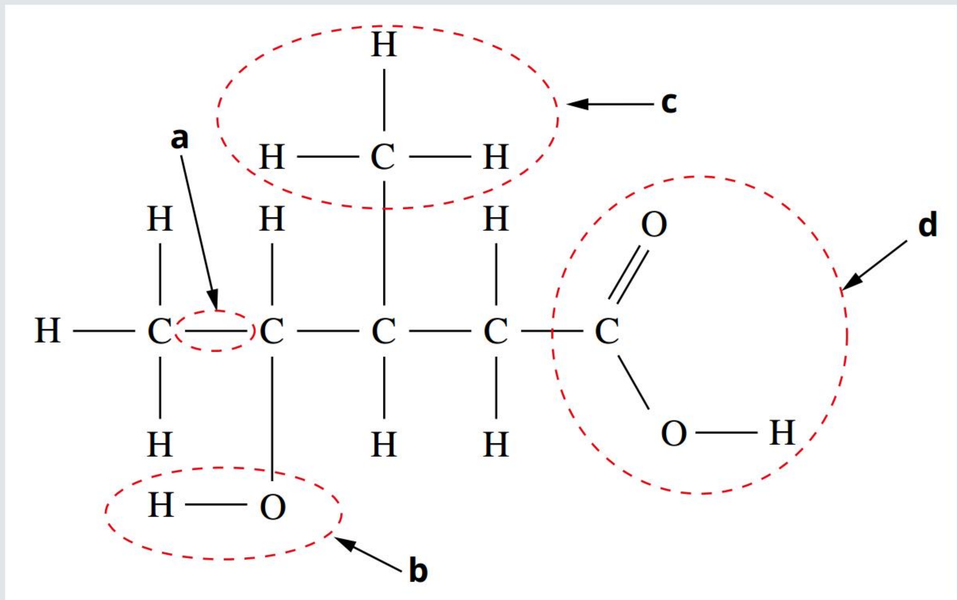
4 Select possible products that might be formed when an unsaturated molecule undergoes an addition reaction with hydrogen gas, halogen gas, water or hydrogen halide.

A IV and V
B I and III
C V and VI
D II and VI

5 Identify two molecules that are necessary for amide production.

6 Identify a product that might be formed when a haloalkane undergoes an elimination reaction.

7 Identify the structures or functional groups labelled a, b, c and d.



8 Identify which of the following best distinguishes the role of acidified potassium dichromate in organic reactions. It reacts in:

A oxidation reactions by promoting the loss of H atoms
B reduction reactions by promoting the gain of O atoms

C oxidation reactions by promoting both the loss of H atoms and the gain of O atoms

D reduction reactions by promoting both the loss of H atoms and the gain of O atoms.

9 Identify which of the following equations correctly represents the complete combustion of ethanol.

A $CH_3CH_2OH(l) + O_2(g) \rightarrow 2C(s) + 3H_2O(g)$

B $CH_3CH_2OH(l) + 2O_2(g) \rightarrow 2CO(g) + 3H_2O(g)$

C $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

D $CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(g)$

Apply

10 Propene undergoes two separate reactions: reaction 1 to form propanol and reaction 2 to form chloropropane. Determine which of the following statements correctly describes these two reactions.

A Both reactions are substitution reactions; reaction 1 requires water as a reactant and reaction 2 requires hydrogen chloride.

B Both reactions require UV light; they are both substitution reactions.

C Both reactions are addition reactions; reaction 1 requires water as a reactant and reaction 2 requires hydrogen chloride.

D Reaction 1 is a substitution reaction and reaction 2 is an addition reaction; they both require an acid catalyst.

11 Ethene molecules are able to undergo addition reactions because they possess a:

A C=C double bond

B large number of C–H bonds

C similar number of C and H atoms

D similar spatial arrangement of certain H atoms around each C atom.

12 Primary and secondary alcohols undergo oxidation but tertiary alcohols will not. This is because primary and secondary alcohols possess:

A a similar ratio of C:H:O atoms

B at least one C–C multiple bond

C a large number of hydroxyl groups

D the hydroxyl group attached to a carbon that has at least one H bonded to it.

13 Chloroethane (C_2H_5Cl) is a product in the reaction between ethane and chlorine. The equation for the reaction is:

$$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$$

Recall the name of this reaction, explain this name and state the reaction conditions.

14 Construct a balanced chemical equation for each of the following reactions.

a gaseous ethene reacted with gaseous hydrogen chloride

b gaseous propene reacted with hydrogen gas in the presence of nickel and heat

15 Construct equations for the production of:

a propan-2-amine from 2-bromopropane

b chloropropane from propane

c butan-2-ol from but-2-ene.

16 Recall the name of the functional group that will be formed in reactions of the following types of alcohols with acidified potassium permanganate solution. (If there is more than one possible product, state both names.)

a primary alcohol

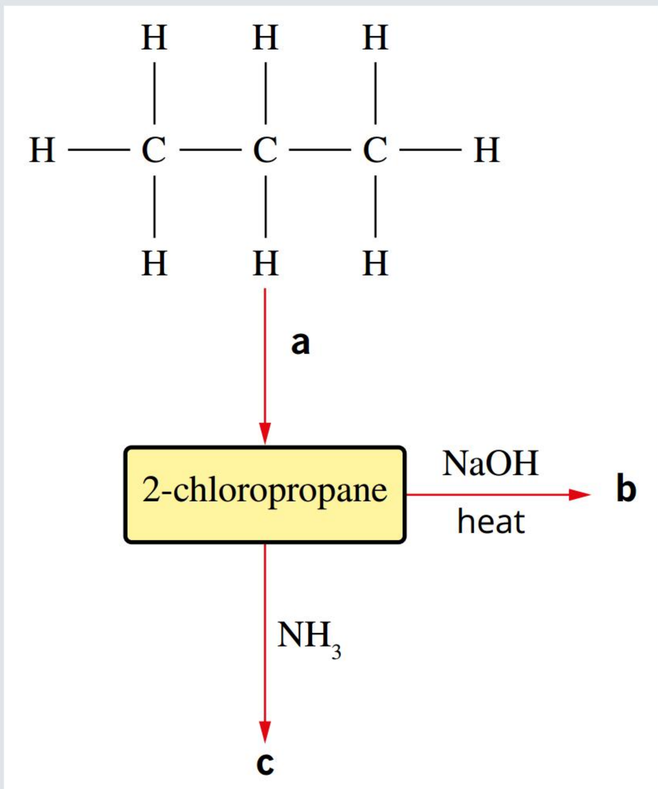
b secondary alcohol

c tertiary alcohol

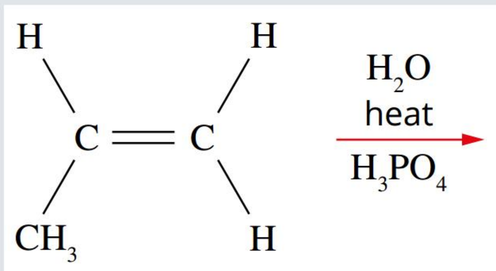
17 Identify the different reactions of alkenes by completing the following table.

Reactants	Type of reaction	Product(s)
alkene and hydrogen		
alkene and hydrogen bromide		
alkene and water (with a catalyst)		
alkene and bromine		

18 Indicate the correct reagents/products (**a**–**c**) by completing the following flow chart of organic reactions.



19 Show the structural formula for the product of this reaction and state the reaction type.



20 Construct chemical pathways in the form of flow diagrams to describe the preparation of:

a a haloalkane from an alkane

b a carboxylic acid from an alcohol.

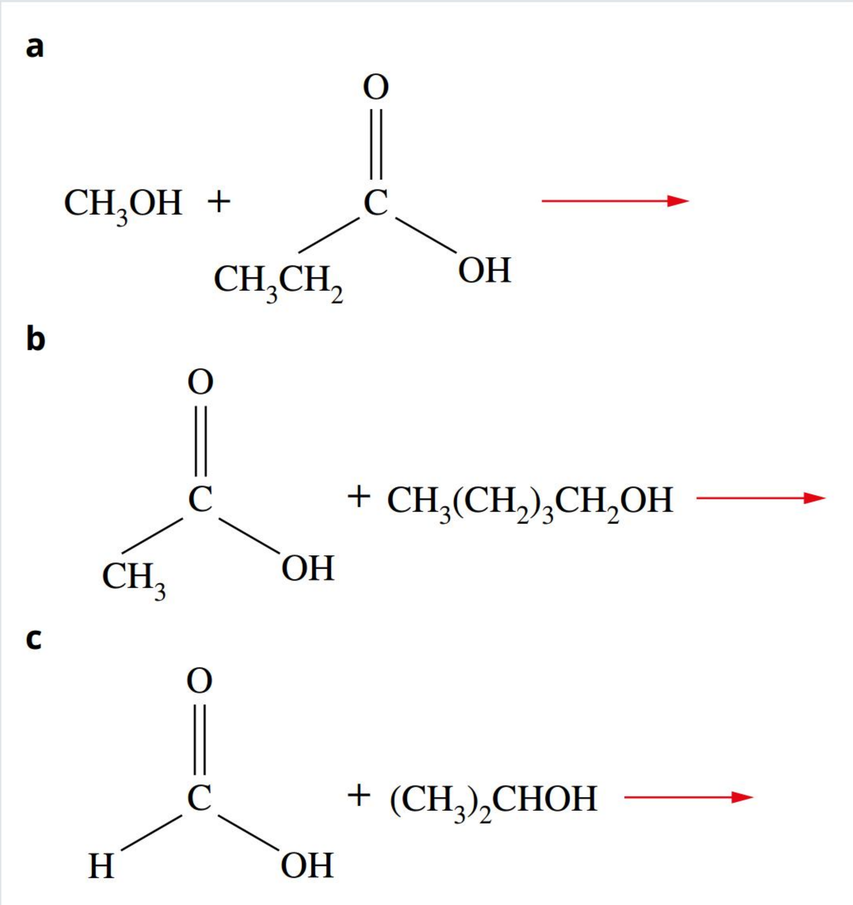
Analyse

21 Construct chemical equations using condensed formulas for the reaction between:

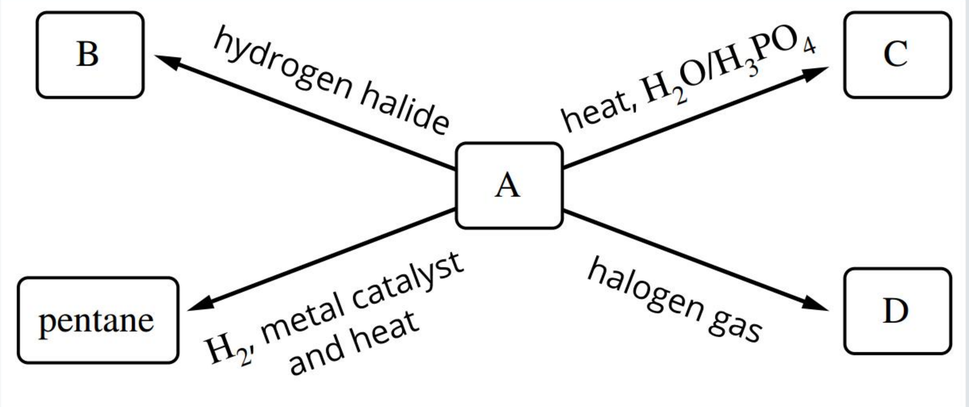
a butane and chlorine

b ethane and oxygen.

22 Identify the product of the following reactions using condensed formulas.



23 Deduce the identities of A–D.



24 Give the condensed formulas for the products of the hydrolysis of each of the following esters when an acid is used as a catalyst.

a methyl ethanoate

b propyl ethanoate

c ethyl methanoate

25 Draw the structural formula of the product that will be formed from the reaction of:

a ethanoic acid and propylamine

b methanamine and methanoic acid

c pentan-3-ol heated with $H^+/Cr_2O_7^{2-}$

d butan-1-ol with $H^+/Cr_2O_7^{2-}$, mild heat; the product is distilled off as it forms.

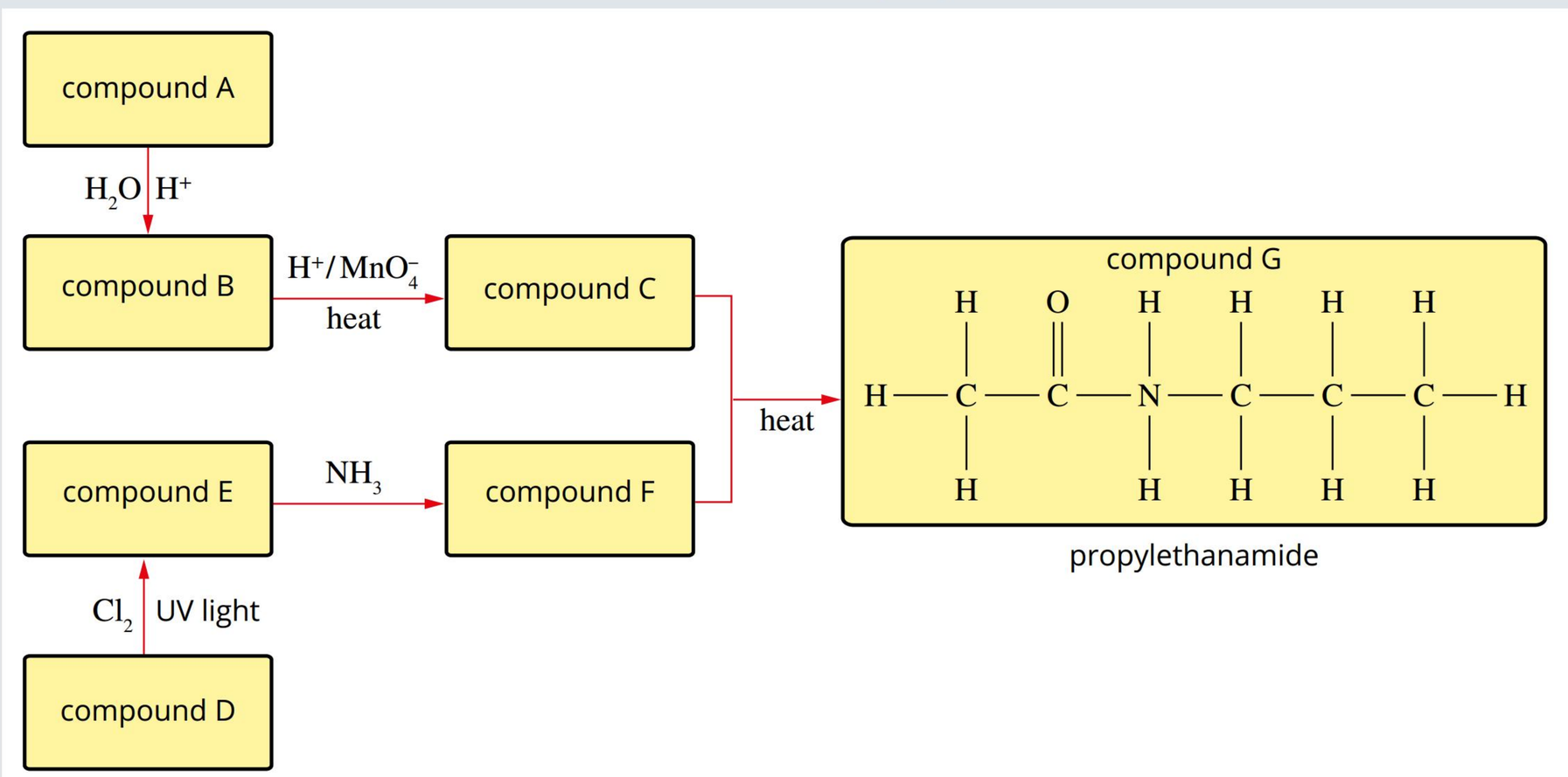
26 Construct a reaction pathway for the synthesis of ethyl ethanoate from an alkene.

27 The reaction pathway shown below leads to the organic compound G.

a Identify the structural formulas of the appropriate compound for A–F and fill in the boxes to complete the pathway.

b Describe a chemical test that could be carried out to distinguish between compounds A and D in the pathway.

c Identify any substitution reactions.



Interpret

28 Propose a reaction pathway that will synthesise:

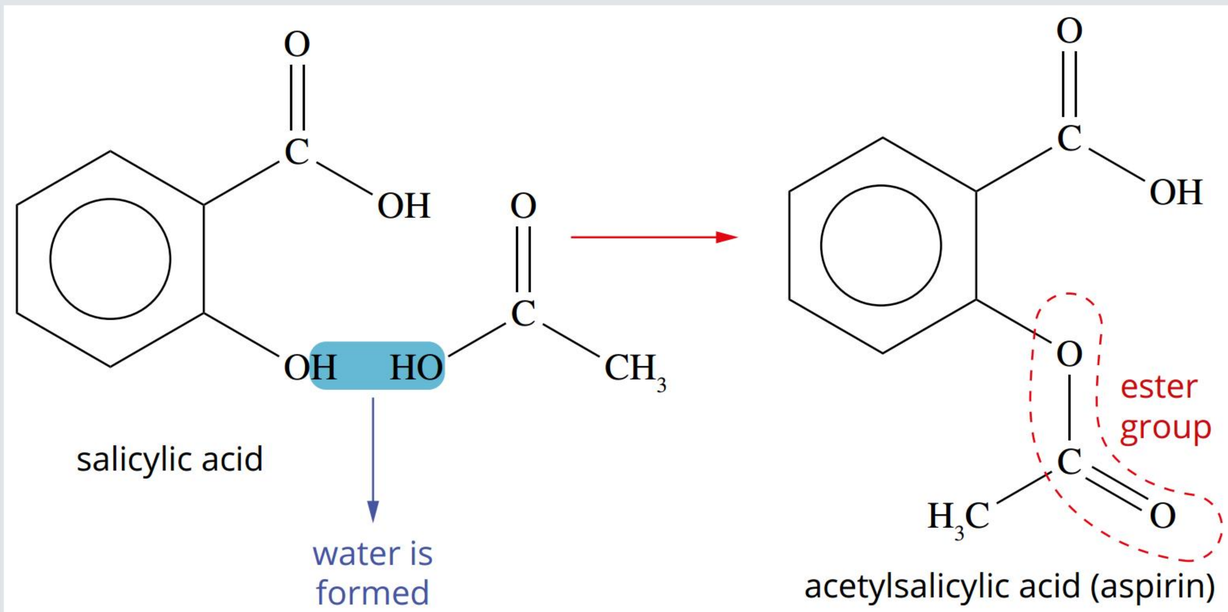
a butanone from butan-2-ol

b butan-2-one from butan-1-ol

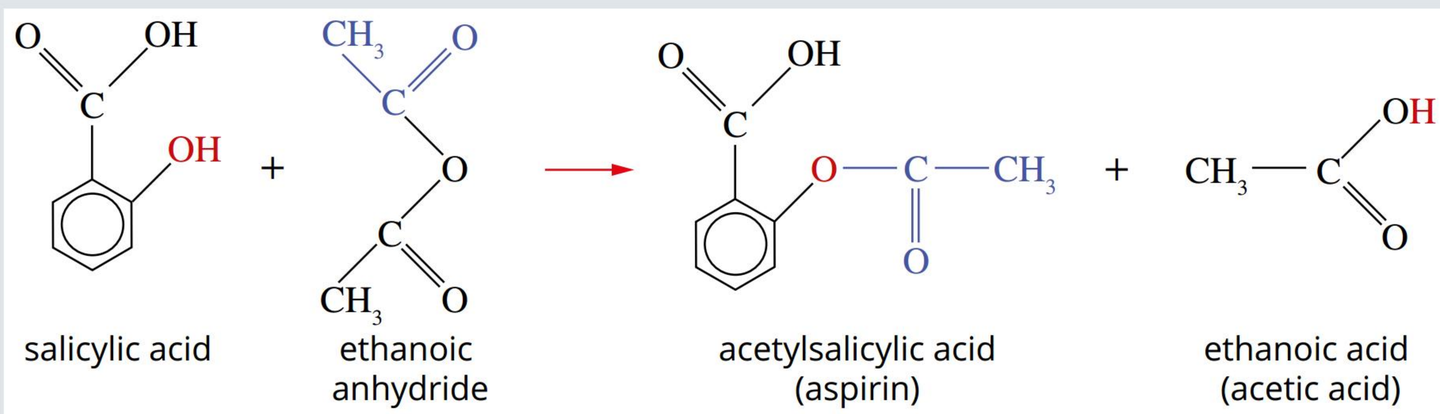
c ethanol from ethene

d propyl methanoate from methanol and propane.

29 Aspirin can be synthesised by an esterification reaction of salicylic acid and ethanoic acid. The process involves a reaction between hydroxyl and carboxyl functional groups to form an ester, according to the pathway shown below.



Although this reaction can be easily carried out in a laboratory, the yield is quite low. Another reaction (shown below) using salicylic acid and ethanoic anhydride is used to produce a greater yield.



Research both of these processes and evaluate their similarities and differences.

Data analysis

DATA SET 1

The information below applies to Questions 1–6.

In an organic chemistry practical unit of work, students completed three chemical reactions and two diagnostic tests. Reactions 1–3 produced compounds A–D. Tests 1 and 2 analysed some of these compounds.

Reaction	Reactant(s)	Reagents/conditions	Product(s)
1	propene	$H_2SO_4/H_2O(g)$	A (minor product) B (major product)
2	A	Oxidising agent, heat/reflux	C
3	C, butanol		D

Results of diagnostic testing

	propene	A
test 1	Colour change	No colour change

	A	B	C
test 2	Neutral pH	Neutral pH	Low pH

Question 1 (2 marks)

Identify tests 1 and 2.

Question 2 (1 mark)

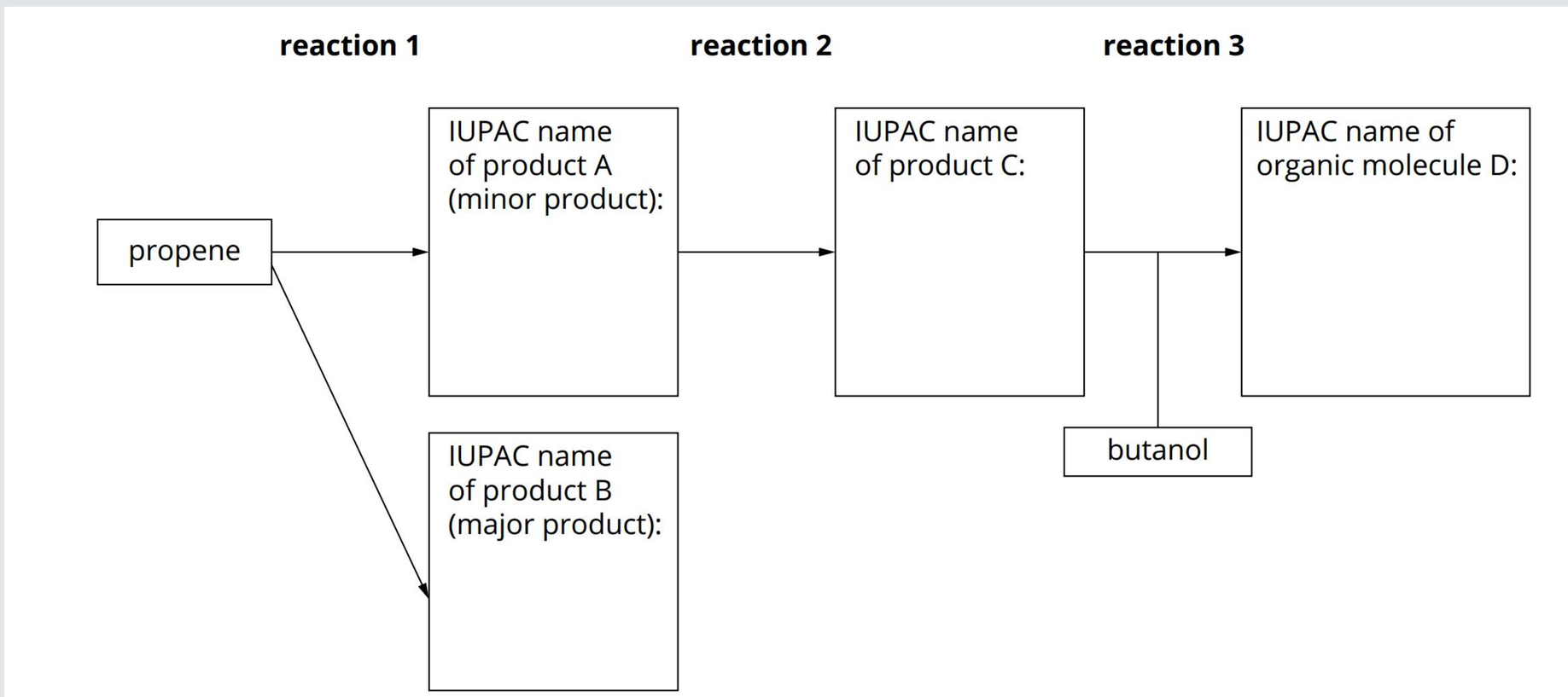
Name reaction 1.

Question 3 (1 mark)

Name the oxidising agent and reaction conditions used in reaction 2.

Question 4 (4 marks)

Identify how compound D is produced by completing the diagram below and naming compounds A–D.



Question 5 (2 marks)

Name reaction 3 and identify a further product of the reaction (other than molecule D).

Question 6 (2 marks)

Organic molecules derived from fossil fuels are used as feedstock for the production of plastics (synthetic polymers). Describe this reaction and indicate which of the above molecules is required.

CHAPTER

10 Organic materials: synthesis, structure and function

Living things are dynamic systems for the production and breakdown of molecules. Thousands of reactions are occurring every second in each body cell. Polypeptides (proteins) and polysaccharides (carbohydrates) are categories of organic chemicals that involve the formation of large molecules from the repeated reaction between smaller, building block units. You eat proteins to supply your body with the materials it needs for growth and repair, and you consume carbohydrates to supply the energy required for movement and biochemical reactions.

Scientists can also synthesise large molecules called polymers from repeated reactions between smaller units. Polymers (commonly called plastics) offer an almost limitless variety of properties, enabling them to be used for many different purposes such as toys, packaging and utensils.

In this chapter, you will learn about:

- the characteristics of the molecules used to build larger molecules
- the structural characteristics of the larger molecules formed.

You will learn that scientists are able to utilise their understanding of the link between molecule structure and properties to design and modify polymers for a multitude of everyday applications.

Syllabus subject matter

Topic 1 • Properties and structure of organic materials

ORGANIC MATERIALS: STRUCTURE AND FUNCTION

- Describe the structural features of
  - amino acids, tripeptides, monosaccharides and disaccharides **10.1**
  - polyethene (LDPE and HDPE), polypropene (syntactic, isotactic and atactic) and polytetrafluoroethene (Teflon) **10.4**
  - polylactic acid (PLA), polyamide (nylon) and polyester. **10.4**
- Explain how properties, including strength, density and biodegradability of polymers, can be related to the structures of the materials. **10.5**
- Explain the acid–base properties of 2-amino acids, including the formation of zwitterions. **10.1**

Topic 2 • Chemical synthesis and design

MACROMOLECULES: POLYMERS, PROTEINS AND CARBOHYDRATES

- Describe, using equations, how
  - addition polymers, including polyethene (LDPE and HDPE), polypropene and polytetrafluoroethene, can be produced from their monomers **10.4**
  - condensation polymers, including polysaccharides (carbohydrates), polylactic acid (PLA), polyamide (proteins and nylon) and polyester, can be produced from their monomers. **10.4**
- Apply amino acid symbols to construct and name tripeptides. **10.2**
- Identify that tripeptides are formed when amino acid monomers are joined by peptide bonds. **10.2**
- Identify that disaccharides are formed when monosaccharides monomers are joined by glycosidic bonds. **10.3**

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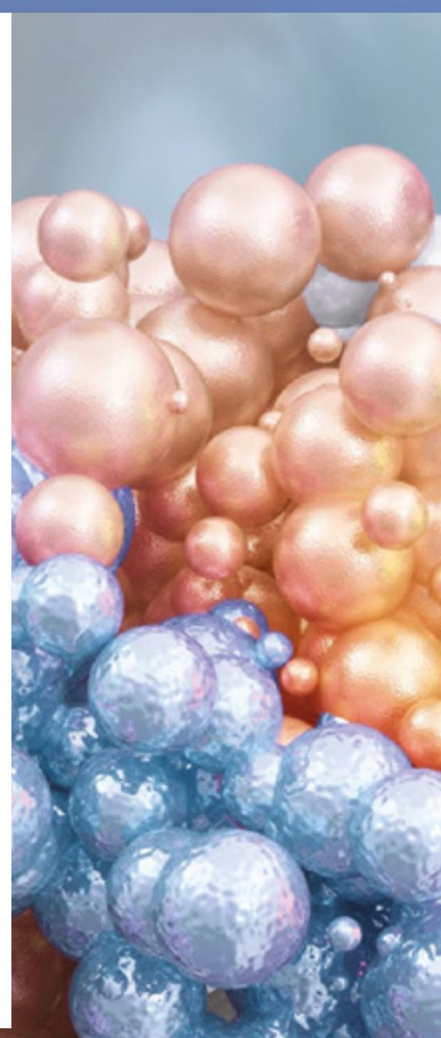
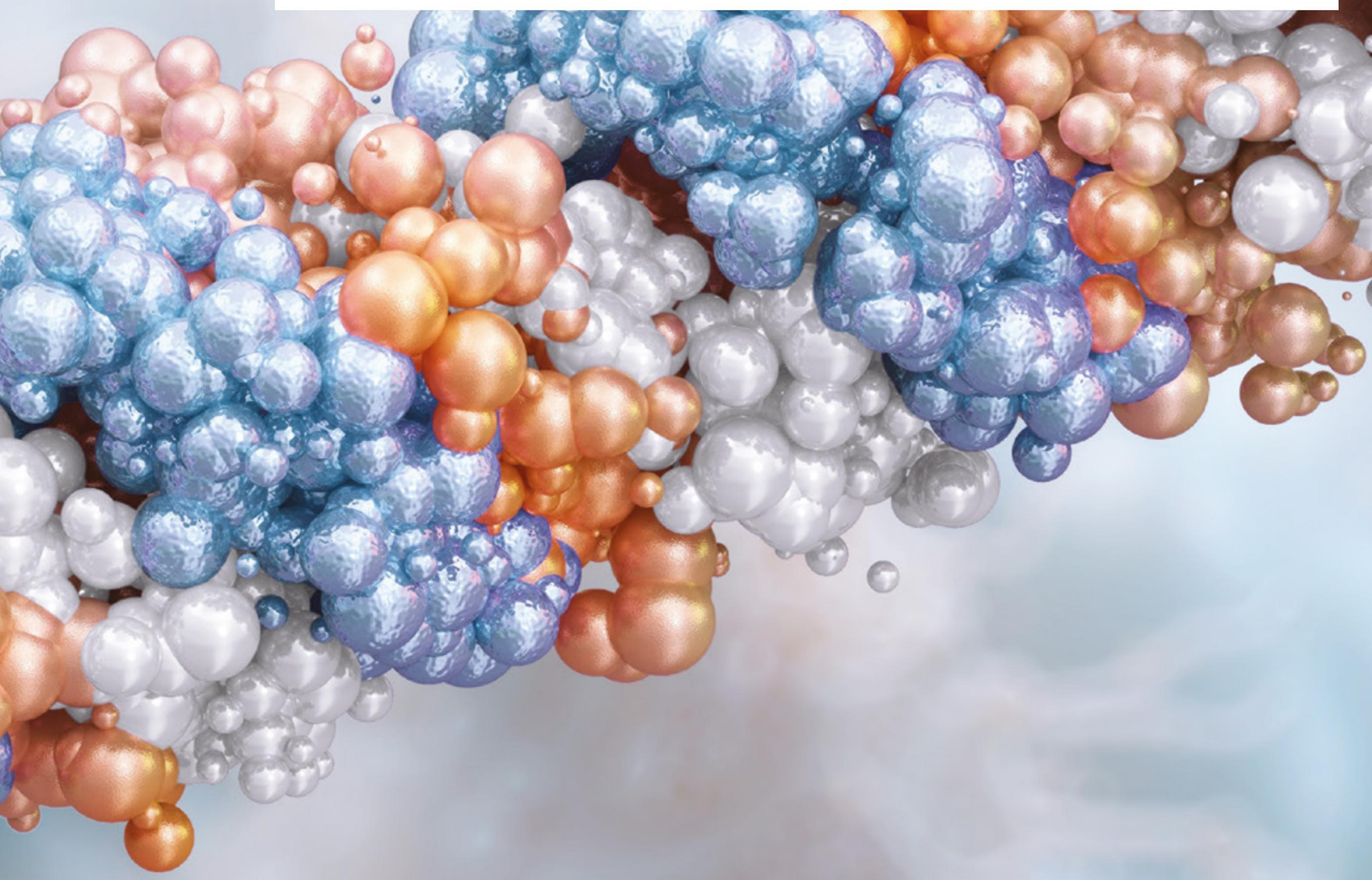
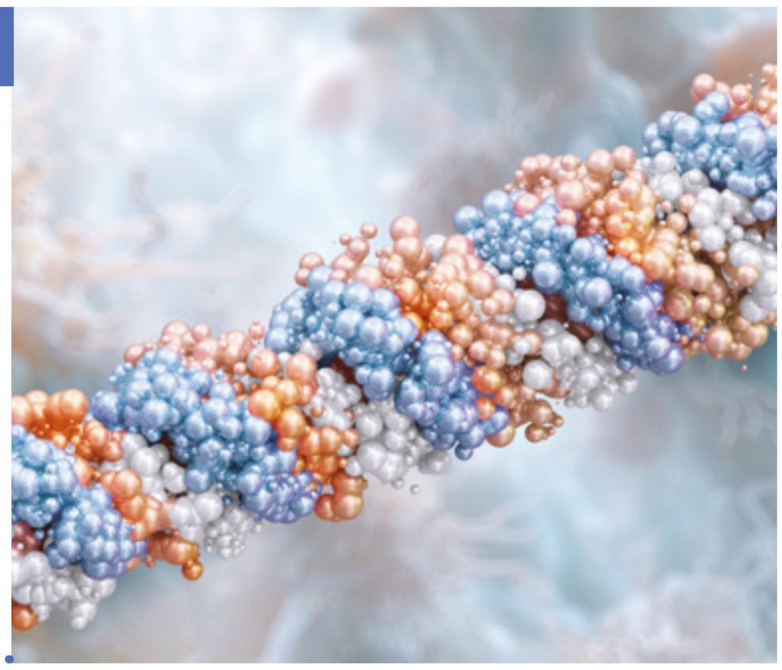




10.1 Amino acids – structure and function

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- recognise and draw the general structure for a 2-amino acid (α-amino acid)
- recognise a 2-amino acid from its structure
- understand that the side chain in a 2-amino acid can be polar or non-polar and recognise polar and non-polar side chains
- understand that the side chain in a 2-amino acid can be acidic or basic and recognise acidic and basic side chains
- recognise a zwitterion
- understand that the structure of an amino acid in a solution depends upon the pH of the solution.



In this module, you will investigate the structure and properties of amino acids. Amino acids are the building blocks that make the thousands of different **polypeptides** and **proteins** that are essential to life.

Polypeptides and proteins have many important functions in living things. These include:

- hormones that control biological processes
- antibiotics that protect bacteria
- enzymes that catalyse specific biochemical reactions
- structural components in cell membranes, muscles, hair, feathers and spider silk (Figure 10.1.1)
- transport of substances across cell membranes or around the body; for example, haemoglobin is found in red blood cells (Figure 10.1.2) and binds to oxygen
- antibody molecules of the immune system.

FIGURE 10.1.1 A spider's web is formed from threads of spider silk, spun from a strong fibrous protein called fibroin.

FIGURE 10.1.2 Red blood cells are biconcave disc-shaped cells that transport oxygen from the lungs to body cells. They contain the protein haemoglobin, which is able to bond reversibly to oxygen molecules.

> The prefix 'mono-' means one only, or single. Therefore, the prefix 'poly-' means many. A polypeptide is formed when many smaller molecules, amino acids, combine. Proteins are long polypeptide molecules.

Plants can manufacture all the **amino acids** required to make polypeptides. They create amino acids from simple inorganic ingredients—such as carbon dioxide, water and nitrates—obtained from the atmosphere and soil. However, animals cannot manufacture all of the amino acids. Animals obtain the amino acids they cannot make themselves from the plant and animal proteins in the food they eat.

STRUCTURE OF AMINO ACIDS

There are 20 different amino acids that make up all the polypeptides in the human body. Every amino acid has an amino functional group ($-NH_2$), a carboxyl functional group (–COOH) and a hydrogen atom attached to a central carbon called the α-carbon (alpha-carbon).

Two of the simplest amino acids are glycine and alanine. The structures of these two molecules are shown in Figure 10.1.3.

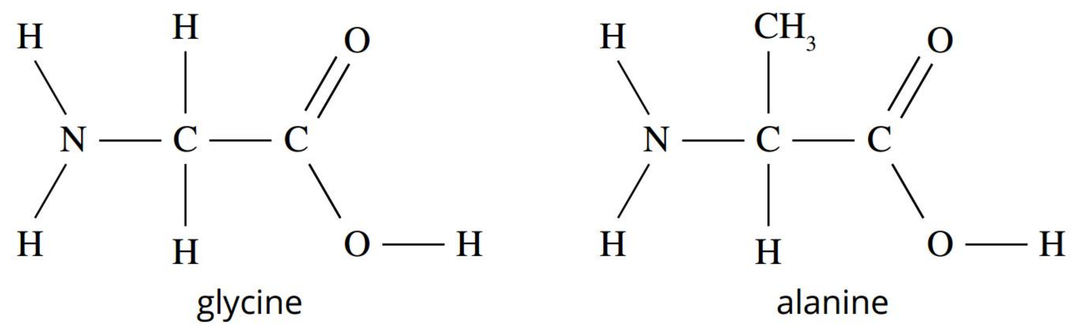


FIGURE 10.1.3 The structures of amino acids glycine and alanine

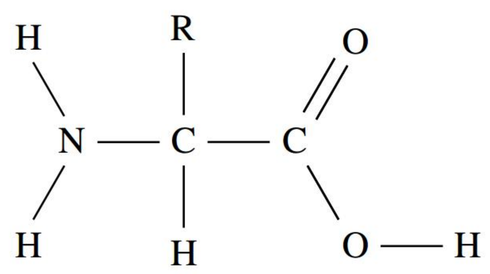


FIGURE 10.1.4 General structural formula of an amino acid. Different amino acids have different groups of atoms as the R group.

General formula of amino acids

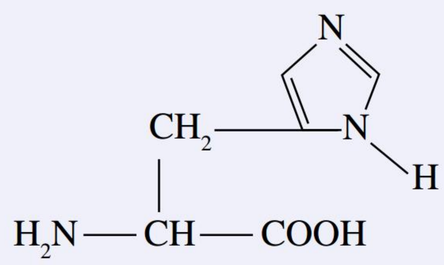
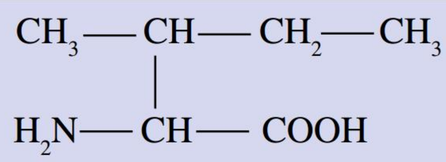
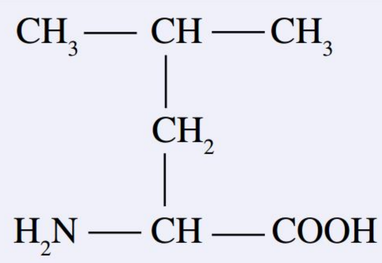
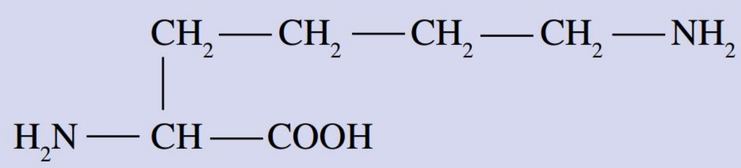
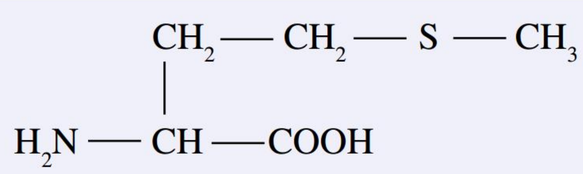
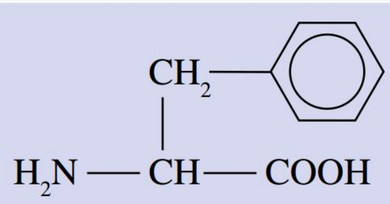
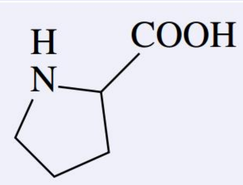
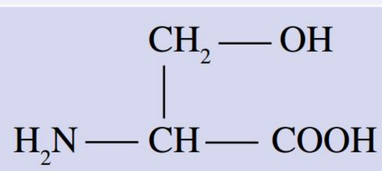
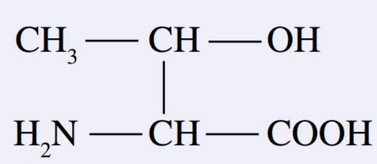
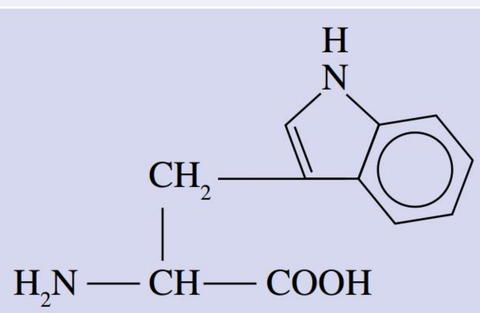
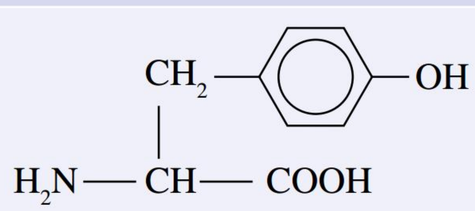
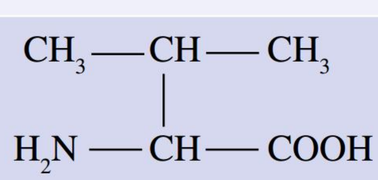
The amino acids used to produce the polypeptides in the human body have the general formula $H_2N–CH(R)–COOH$, shown as a structural formula in Figure 10.1.4.

Amino acids are known as **2-amino acids**. This is because the carbon atom of the carboxyl group is numbered as the first carbon in the chain (according to IUPAC rules) and the amino group is bonded to the carbon atom adjacent to it, numbered '2' in the chain. 2-amino acids are also called α-amino acids.

The 20 2-amino acids used to make human polypeptides are listed in your Formula and Data book, pages 12–15, and are shown in Table 10.1.1, along with the three-letter abbreviations commonly used for them by biochemists.

TABLE 10.1.1 Amino acids found in the human body, with their three-letter abbreviations and R groups

Name	Symbol	Structure
alanine	Ala	$H_2N—CH(CH_3)—COOH$
arginine	Arg	$H_2N—CH(CH_2—CH_2—CH_2—NH—C(=NH)—NH_2)—COOH$
asparagine	Asn	$H_2N—CH(CH_2—C(=O)—NH_2)—COOH$
aspartic acid	Asp	$H_2N—CH(CH_2—COOH)—COOH$
cysteine	Cys	$H_2N—CH(CH_2—SH)—COOH$
glutamine	Gln	$H_2N—CH(CH_2—CH_2—C(=O)—NH_2)—COOH$
glutamic acid	Glu	$H_2N—CH(CH_2—CH_2—COOH)—COOH$
glycine	Gly	$H_2N—CH_2—COOH$

histidine	His	
isoleucine	Ile	
leucine	Leu	
lysine	Lys	
methionine	Met	
phenylalanine	Phe	
proline	Pro	
serine	Ser	
threonine	Thr	
tryptophan	Trp	
tyrosine	Tyr	
valine	Val	

Amino acids are commonly given three-letter abbreviations. For example, alanine is represented by Ala and glycine is represented by Gly.

Properties of R groups in amino acids

The major difference between one amino acid and another is the group of atoms that make up the **side chain**. This side chain is represented in the general structure as an **R group**. The side chain may be:

- non-polar (e.g. $-CH_3$ in alanine and $-CH(CH_3)_2$ in valine)
- polar (e.g. $-CH_2COOH$ in aspartic acid and $-CH_2OH$ in serine).

  The side chain may also include functional groups that can behave as:
- proton donors (e.g. $-CH_2COOH$ in aspartic acid contains an acidic carboxyl group)
- proton acceptors (e.g. $-CH_2CH_2CH_2CH_2NH_2$ in lysine contains a basic amino group).

ESSENTIAL AND NON-ESSENTIAL AMINO ACIDS

Within the cells in their bodies, humans can synthesise 11 of the 20 amino acids required to make polypeptides and proteins. However, the other nine amino acids (isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, valine and histidine, in the case of infants) must be obtained directly through the proteins we eat. This is because human cells do not have the capacity to produce them.

These nine amino acids are known as **essential amino acids**. A healthy diet should include proteins that contain these essential amino acids. The human body does not store amino acids, so a balanced intake of protein is required each day. Lack of amino acids in the diet can cause serious diseases, such as kwashiorkor, as shown in Figure 10.1.5. 'Kwashiorkor' means 'rejected one' in the Ga language of coastal Ghana where the disease is common. It reflects the incidence of the disease in children who have been weaned from breast milk to a diet that is high in carbohydrates and lacking in protein.

FIGURE 10.1.5 This child is suffering from kwashiorkor, which is a form of malnutrition caused by a protein-deficient diet.

A balanced diet

Proteins from animal sources contain all the essential amino acids. As Table 10.1.2 shows, vegetable proteins are often deficient in one or more essential amino acids. For example, corn is too low in lysine and tryptophan to support normal growth in young children.

TABLE 10.1.2 Foods deficient in one or more of the nine essential amino acids

Food	Amino acid deficiency
legumes	methionine
soybeans	methionine
corn	lysine, tryptophan
nuts	methionine
wheat	lysine

For this reason, vegetarians must ensure that their diets contain **complementary proteins**. This means that instead of eating plant protein from a single source, vegetarians should eat a variety of plant foods. Deficiencies of amino acids in one plant can then be supplemented by the amino acids present in another. For example, rice and lentils contain complementary proteins. In Asia, rice and lentils have been part of the staple diet for thousands of years. In developed countries, people usually get all the amino acids they require by eating complementary proteins.

THE ACID-BASE PROPERTIES OF AMINO ACIDS

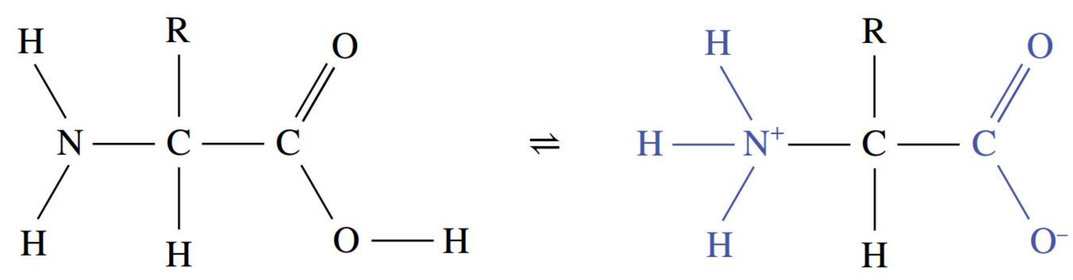
Amino acids are difunctional—they contain an amino group and a carboxylic acid group. The presence of these two groups in their structure means amino acids are amphoteric—they can react as either acids or bases, depending on the circumstances. The nature of its side chain (R group) can also affect the acid–base properties of an amino acid.

Amino acids as zwitterions

Amino acids contain polar amino and carboxyl functional groups. Therefore, amino acids can form hydrogen bonds with water molecules and are soluble in water. In solution, the:

- $–NH_2$ group can act as a base, accepting a proton to become a $–NH_3^+$ group
- –COOH group can act as an acid, donating a proton to become a $–COO^–$ group.

As a result, an amino acid molecule in an aqueous solution may be in the form $^+H_3N–CH(R)–COO^–$. Such a molecule is shown in Figure 10.1.6 and is called a **zwitterion** or **dipolar ion**. Note that the zwitterion has two oppositely charged groups but the overall charge on the molecule is neutral.



The carboxyl group of an amino acid can act as an acid, donating a proton to the amine group.

This alternate form of the amino acid is a zwitterion.

FIGURE 10.1.6 An amino acid can exist in equilibrium with its zwitterion.

> A zwitterion is a dipolar form of an amino acid that contains positive and negative charges but has no charge overall.

Acid–base properties

The dual acidic and basic nature of amino acids means that different chemical forms of an amino acid can be in equilibrium in a solution. The predominant form depends on the pH of the solution and the particular amino acid concerned. In the examples below, 'low pH' means a pH below the isoelectric point of the particular amino acid (refer to pages 12–15 of the Formula and Data book) and 'high pH' means a pH above the isoelectric point of the particular amino acid (Formula and Data book):

- At intermediate pH (typically pH 5–7), the zwitterion $^+H_3N–CH(R)–COO^–$ is most abundant.
- At low pH, the cation $^+H_3N–CH(R)–COOH$ is most abundant. The H_3O^+ ions in solution can react with the amino acid according to the equation:

$$^+H_3N–CH(R)–COO^–(aq) + H_3O^+(aq) \rightleftharpoons {}^+H_3N–CH(R)–COOH(aq) + H_2O(l)$$

If the concentration of $H_3O^+(aq)$ is very high (as it is in a solution of low pH), the position of this equilibrium lies well to the right.

- At high pH, the anion $H_2N–CH(R)–COO^–$ is most abundant. The $OH^–$ ions in solution can react with the amino acid according to the equation:

$$^+H_3N–CH(R)–COO^–(aq) + OH^–(aq) \rightleftharpoons H_2N–CH(R)–COO^–(aq) + H_2O(l)$$

If the concentration of $OH^–(aq)$ is very high (as it is in a solution of high pH), the position of this equilibrium lies well to the right.

As you can see in Figure 10.1.7, the charge on the predominant form of the amino acid depends on the pH of the solution.

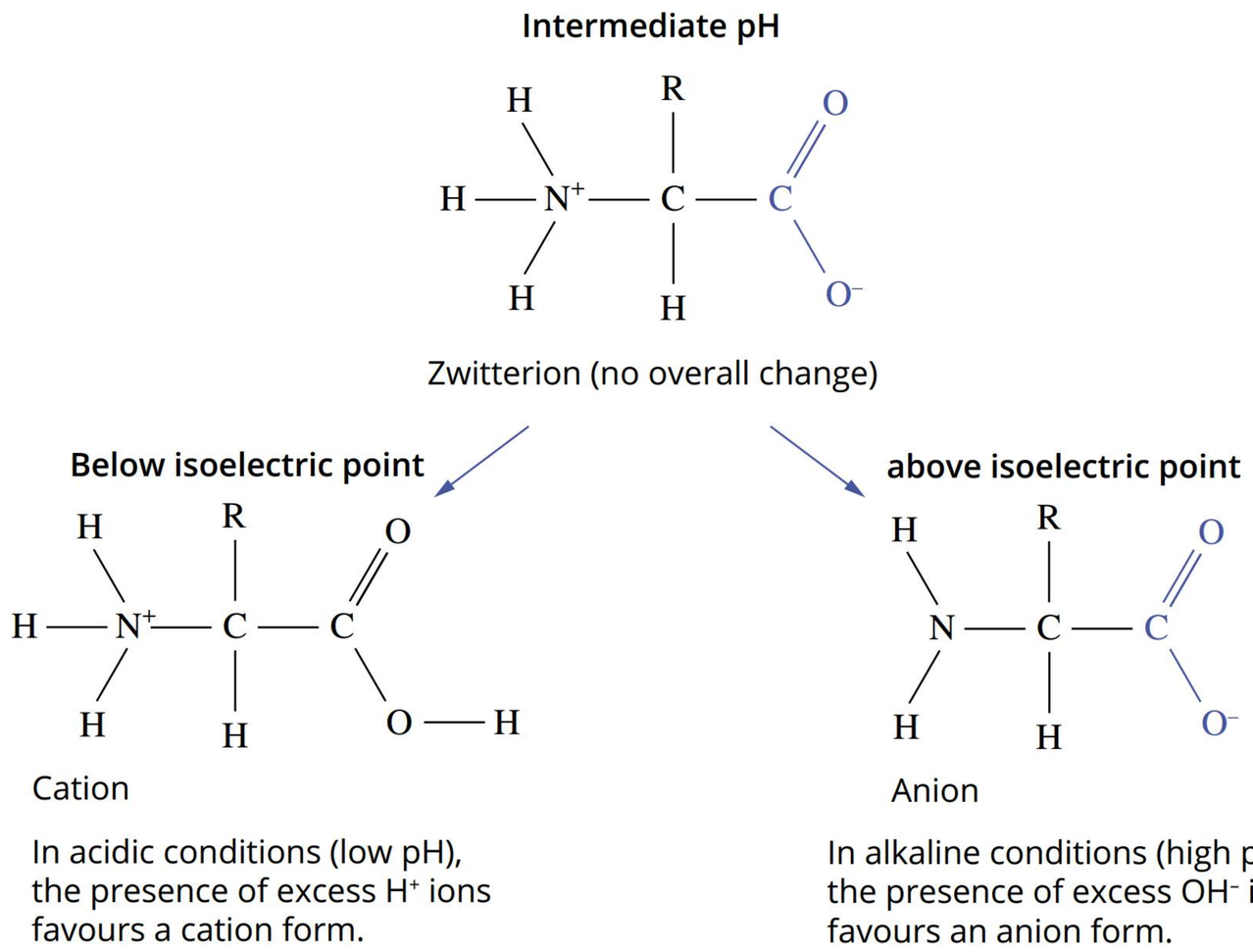


FIGURE 10.1.7 Amino acids at low and high pH conditions

The form that a particular amino acid will take at a particular pH value can be determined from what is called its **isoelectric point**. Each amino acid has a pH where the zwitterion is the favoured form and the positive and negative charges are balanced. This is the isoelectric point. The isoelectric point of each amino acid is unique, as they all have different structures and different acid–base properties. Values for the 20 standard amino acids range from as low as 2.77 to as high as 10.76.

As an example, the isoelectric point of glycine is 6.1. At pH 6.1, it will exist primarily as the zwitterion. At pH lower than 6.1 (in the presence of acid), it will exist in the anion form. At pH higher than 6.1, it will exist in the cation form. The three forms are shown in Figure 10.1.8.

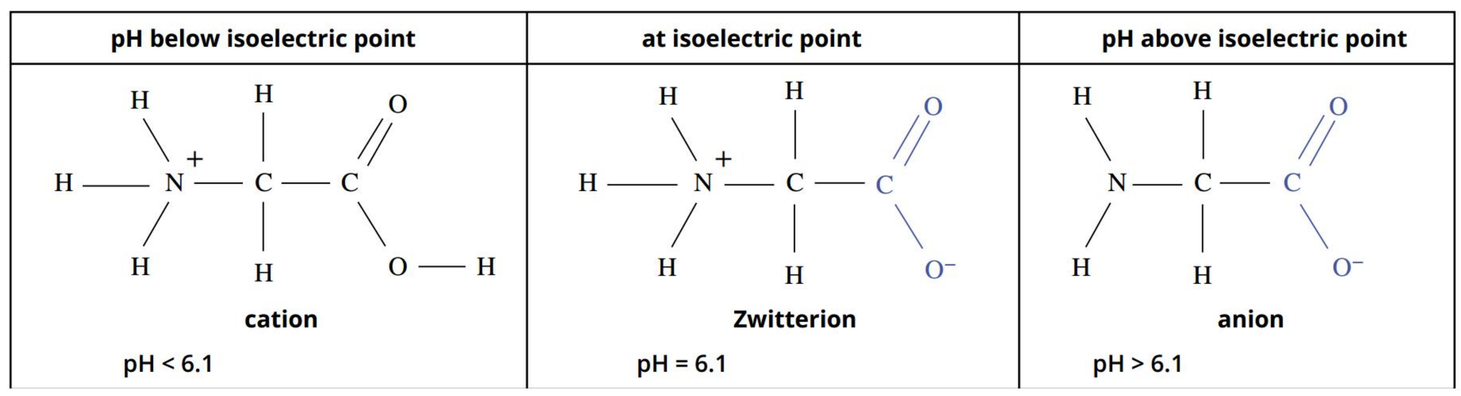


FIGURE 10.1.8 Glycine at different pH values

> Amino acids have an isoelectric point, where the positive and negative charges are balanced. Below the isoelectric point, the amino acid forms a cation. Above the isoelectric point, the amino acid forms an anion.

Effect of the R group on the acid–base properties of amino acids

If the R group contains a functional group with acid–base properties, it is possible for other charged structures of the amino acid to form. For example, at a pH of 12, the predominant form of aspartic acid is an ion with a charge of 2– (Figure 10.1.9). On the other hand, at a pH of 2, lysine exists predominantly as an ion with a charge of 2+ (Figure 10.1.10).

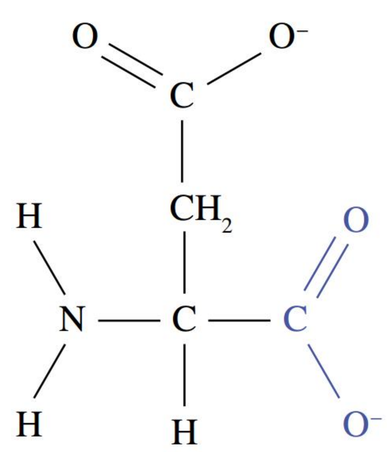


FIGURE 10.1.9 The structure of aspartic acid at pH 12 showing that it has a charge of 2–

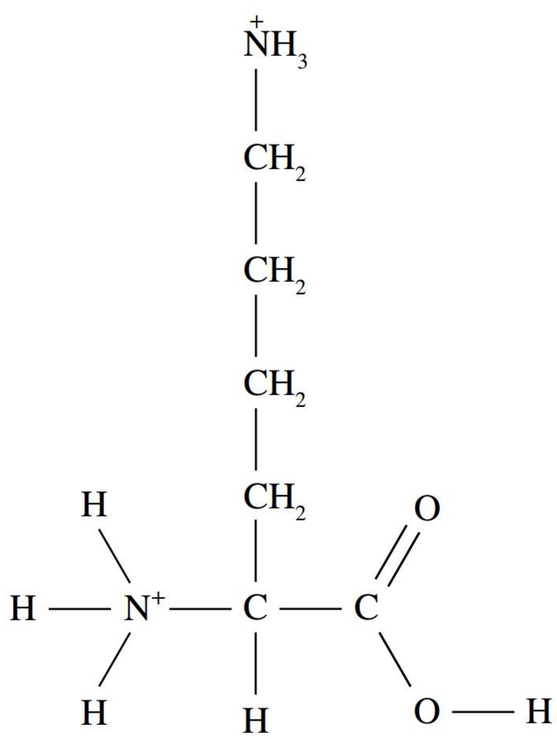
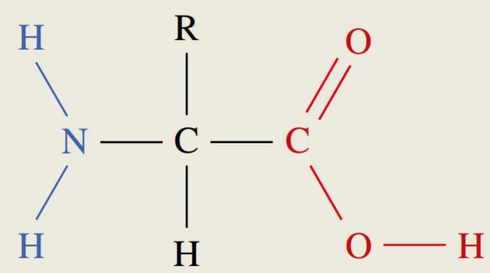


FIGURE 10.1.10 The structure of lysine at pH 2 showing that it has a charge of 2+

10.1 Review

SUMMARY

- 2-amino acids have the structure shown in the following figure.



- Amino acids contain a carboxyl group (highlighted in red), an amino group (highlighted in blue), a hydrogen atom and a side chain called the R group, all bonded to the same carbon atom.
- There are 20 different amino acids found in human proteins.
- The nine essential amino acids must be provided directly through the proteins in the diet, as human cells cannot produce them.
- Non-essential amino acids can be manufactured in the body from other dietary components.
- Three-letter abbreviations are commonly used to represent an amino acid.
- The R group, also known as the side chain, may be a non-polar group of atoms or a group of atoms that includes a polar functional group. The R group may also exhibit acid–base properties.
- Zwitterions are present in crystalline salts of amino acids and also in amino acid solutions of intermediate pH.
- An amino acid is present in cationic form in solutions of low pH and in anionic form in solutions of high pH.
- The form an amino acid takes at a particular pH is determined by its isoelectric point. The isoelectric point is the pH at which the positive and negative charges of an amino acid are balanced.
- Each amino acid has a unique isoelectric point.

KEY QUESTIONS

Describe

1 Use Table 10.1.1 on page 400 to find the names of the amino acids with the following three-letter abbreviations.

a Asn
b Tyr
c Asp
d Met

2 Recall the structural features of a 2-amino acid.

3 Recall why essential amino acids should be included in a healthy diet.

4 State the reason why vegetarians must ensure that their diet contains complementary proteins.

5 Refer to the structure of glycine (page 13 of your Formula and Data book) to identify the part of the molecule that:

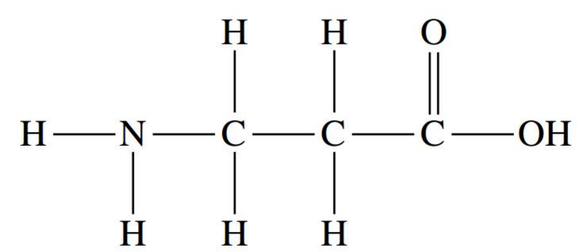
a can act as a base
b can act as an acid.

6 **a** Identify the pH conditions at which 2-amino acids exist as anions. Refer to the amino acid isoelectric point in your response.

b Give the general structure for a 2-amino acid in its anionic form.

Apply

7 Explain why the structure below is not classified as a 2-amino acid.



8 Identify a 2-amino acid that will form an alkaline solution when added to water.

9 Use your understanding of bond polarity and the acid–base properties of functional groups to complete the following table that categorises properties of an amino acid's R group.

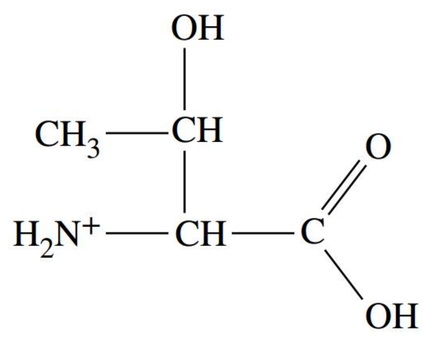
Structure of R group	Is the R group polar or non-polar?	Is the R group acidic, basic or neutral?
$-CH(CH_3)_2$		
$-CH_2COOH$		
$-CH_2C_6H_5$		
$-(CH_2)_4NH_2$		

10 The solubility in water of serine is far higher than that of alanine. Refer to the structure of both molecules to explain why.

Continued over page

10.1 Review *continued*

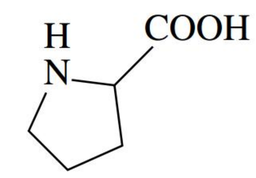
11 Identify the amino acid in the diagram and the likely pH of the solution.



12 Show an equation for the amino acid cysteine forming a cation. Explain the conditions needed for it to form the cation. The zwitterion formula for cysteine is: $^{+}H_3N–CH(CH_2SH)–COO^{-}$.

Analyse

13 Identify the carboxyl group, amino group and R group in proline by circling and labelling the relevant parts of the structure. Classify the R group as polar or non-polar.

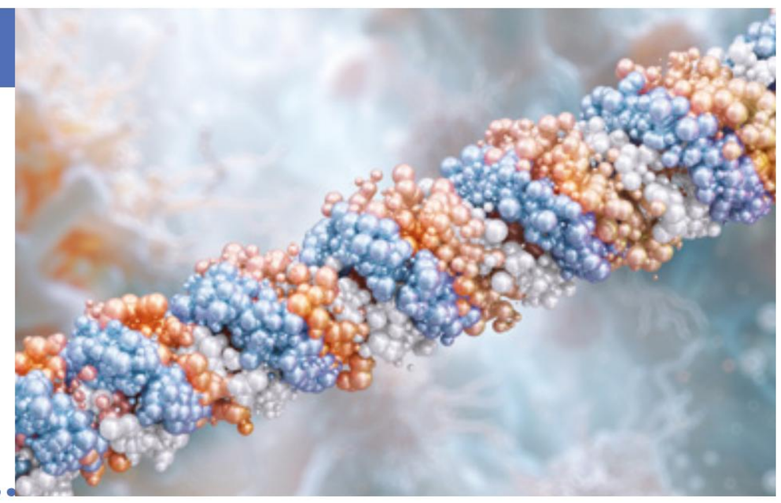


14 Mixtures of amino acids can be separated by a technique called ion-exchange chromatography. In this technique, the mixture flows through a column containing an inert resin that has charged side chains. If a mixture of lysine and glutamic acid in a solution with pH 6 is passed through a column that has resin with negatively charged side chains, the glutamic acid will travel down the column faster and can be collected at the bottom of the column. The lysine will be attracted to the resin. Use Table 10.1.1 on page 400 to compare the structures of lysine and glutamic acid and explain why they can be separated in this way.

10.2 Polypeptides and proteins – formation and structure

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- describe the condensation reaction of 2-amino acids to form polypeptides
- recognise and draw peptide bonds
- recognise and draw the structure of dipeptides and tripeptides
- recognise the 2-amino acids in a polypeptide
- understand that polypeptides are classified as proteins when more than 50 amino acid monomers are joined by peptide bonds.



In this module, you will learn about the chemical reactions of amino acids that produce larger molecules called **polypeptides** and **proteins**. These reactions are examples of condensation reactions.

The molecules in condensation reactions have a pair of functional groups that can react together. When they react, a new functional group is produced that links the molecules. At the same time, a small molecule is also produced. The small molecule is often water, hence the use of the word 'condensation', but some other small molecules are also possible.

In this section, you will learn that the number of amino acids linking in a particular condensation reaction varies. Table 10.2.1 shows that the peptides formed are generally grouped into three categories. When over 50 amino acids combine, the product is considered to be a polymer and the reaction is referred to as a **condensation polymerisation** reaction. (Note: the complexity of molecules in living things means the progression in definition from polypeptide to protein is a fairly loose one.)

TABLE 10.2.1 Classification of polypeptides

Number of amino acids reacting	Category of product formed	Examples
from 2 to 20	peptides such as dipeptides, tripeptides	glutathione
between 20 and 50	polypeptides	dendroaspis natriuretic peptide (DNP)
greater than 50	protein (polyamide)	collagen, insulin

Many biologically important molecules are produced by condensation polymerisation. These molecules include proteins, DNA, **cellulose** and **starch**. Insulin, as shown in Figure 10.2.1, is a small protein made from 51 amino acids. Insulin allows your body to use **glucose** from carbohydrates in your food, either for energy or for storing glucose for future use. Larger proteins are estimated to contain up to 30 000 amino acid residues.

FIGURE 10.2.1 This young girl is injecting herself with insulin to control diabetes. Insulin is one of the many proteins that is formed by the polymerisation of amino acids. Diabetes is a group of diseases associated with abnormally high levels of sugar in the blood.

DIPEPTIDES

As you learnt in Chapter 9, a condensation reaction can occur between a molecule that contains a carboxyl group (–COOH) and a molecule that contains an amino group (–NH_2). An amide functional group (–CONH–) is formed that links the two molecules. A molecule of water is also produced, as shown in Figure 10.2.2.

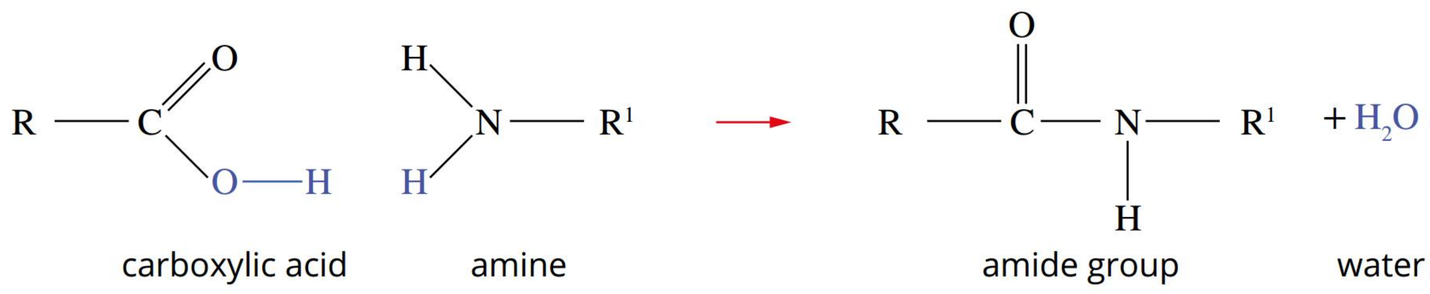


FIGURE 10.2.2 An amide group forms when a carboxyl group reacts with an amino group. A water molecule is also produced.

Because 2-amino acids contain both an amino functional group and a carboxyl functional group, they can undergo **condensation reactions** with each other. When two amino acids react, an amide group, called a **peptide link** (also called a peptide group or peptide bond), is formed, which links the molecules together.

Molecules made from amino acids are often called peptides. When two amino acid molecules react together, as shown in Figure 10.2.3, the product is referred to as a **dipeptide**.

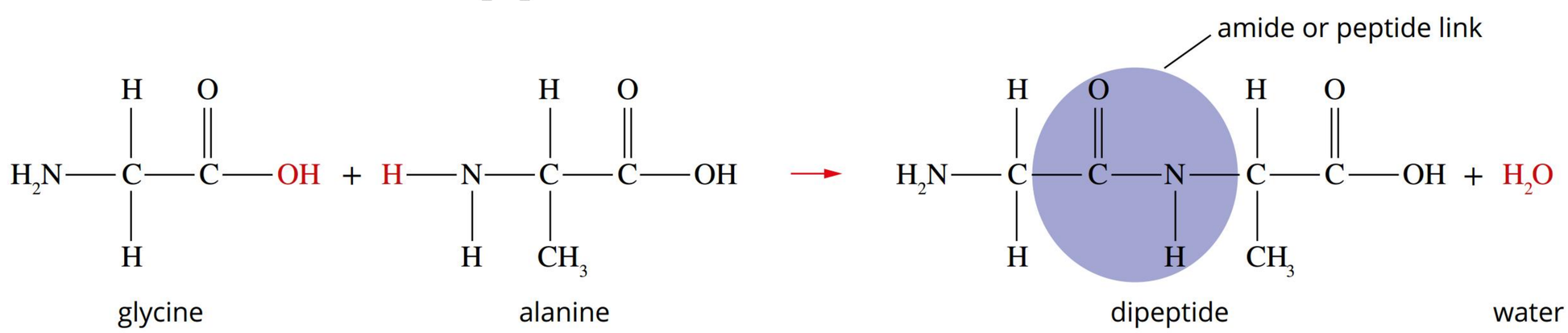


FIGURE 10.2.3 A condensation reaction between two amino acids, glycine and alanine. Note how the carboxyl and amino groups react to form the dipeptide and water.

Each time a pair of different amino acids react in this way, there are two possible product molecules, depending on which ends of each molecule react together (Figure 10.2.4).

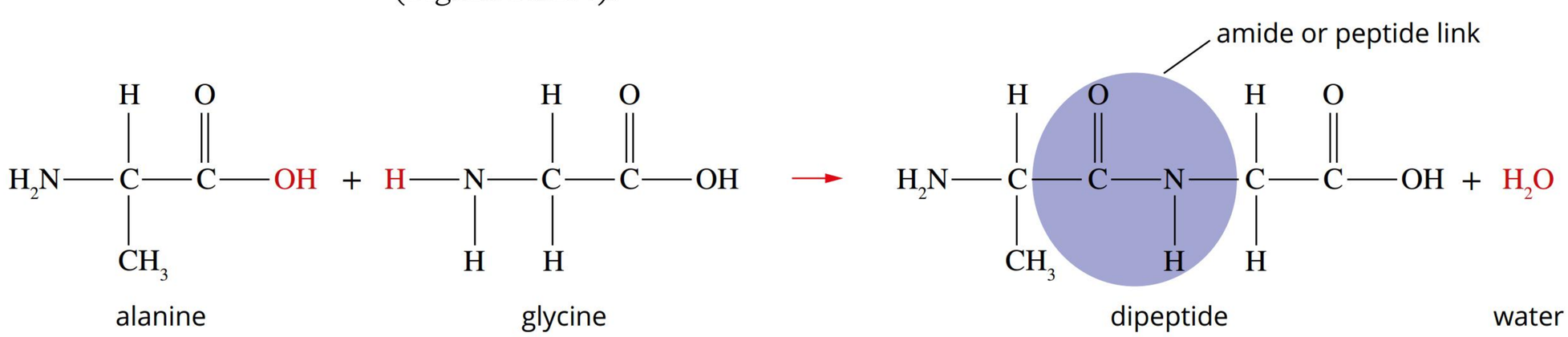


FIGURE 10.2.4 Another dipeptide molecule formed from the reaction between glycine and alanine. Both dipeptides share the same molecular formula but their properties will differ slightly due to the different positions of the R groups.

TRIPEPTIDES

When three amino acid molecules react together, a **tripeptide** is formed. In this condensation reaction, two water molecules and two peptide links are formed. An example of tripeptide formation is shown in Figure 10.2.5.

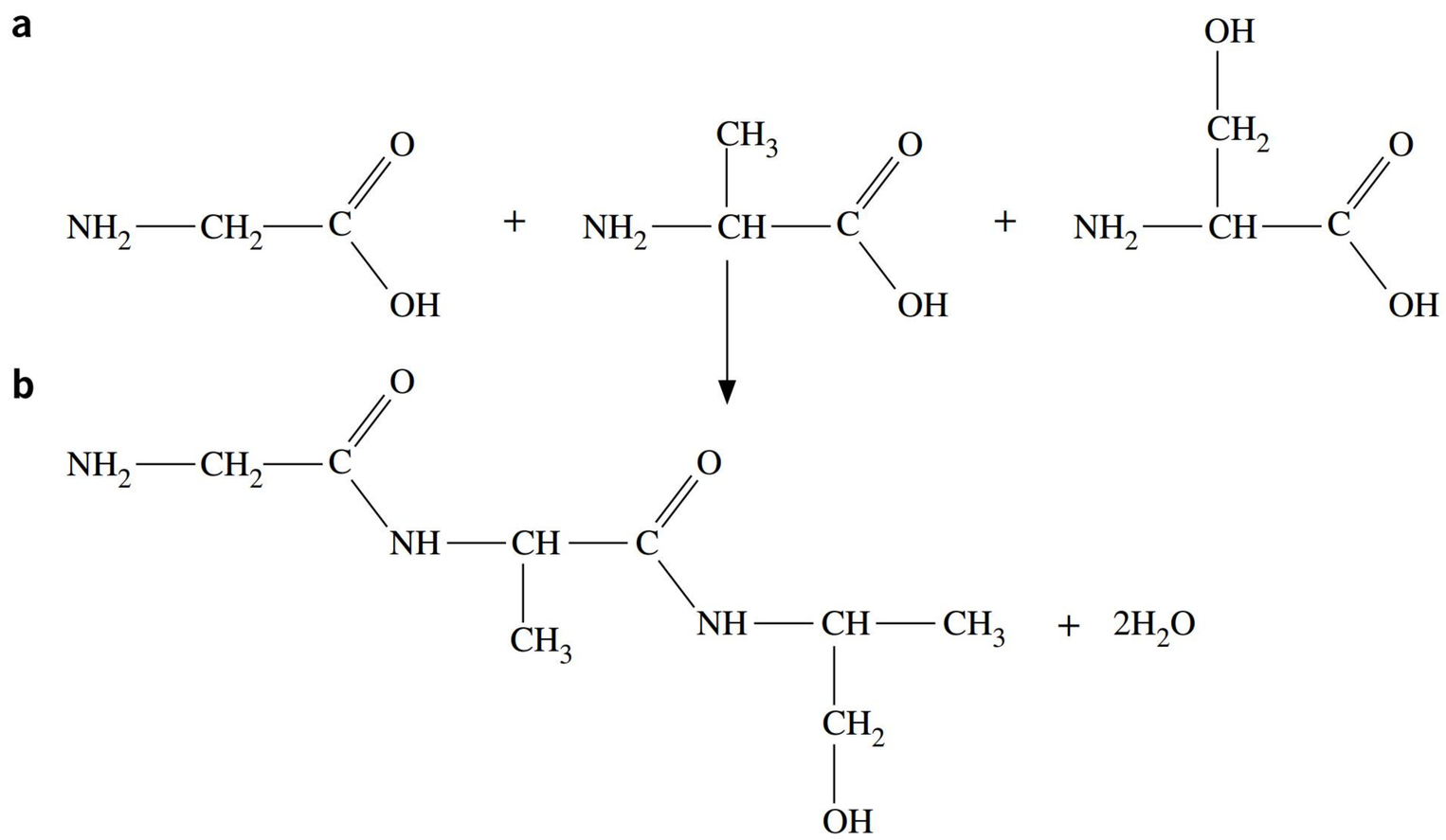


FIGURE 10.2.5 (a) A condensation reaction between three amino acids (b) forms a tripeptide and two molecules of water.

There are several tripeptides that play an important role in living things, the most important one to humans being glutathione (Figure 10.2.6). Glutathione is a powerful antioxidant made in the body's cells. Its levels decrease as a result of ageing, stress and toxin exposure. Boosting glutathione levels can help to reduce the effects of ageing. It is formed from glutamic acid, cysteine and glycine.

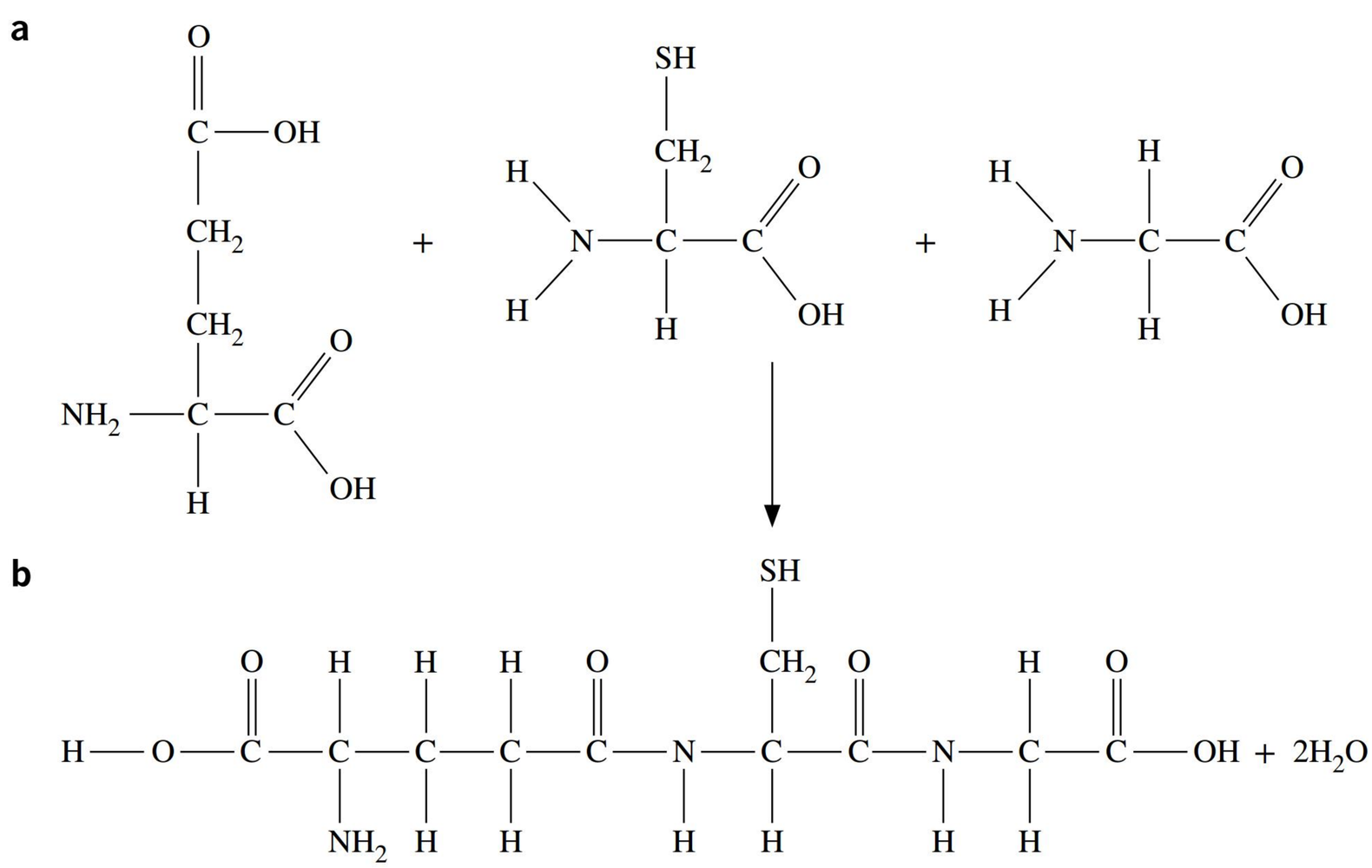


FIGURE 10.2.6 An important tripeptide in living things, glutathione. The three amino acids in glutathione are shown in part **a** of the diagram and the tripeptide formed is shown in part **b**. Note that the peptide bond between glutamic acid and cysteine is formed from the carboxylic acid on the R group of glutamic acid.

Naming peptides

A shorthand notation is often used to describe the amino acid sequence in a peptide, using the three-letter abbreviations of 2-amino acid structures listed in Table 10.1.1 on page 400. By convention, the structure is drawn so the free amino group is on the left and the free carboxyl group is on the right. The tripeptide drawn in Figure 10.2.5 can be represented as Gly-Ala-Ser, while glutathione has the shorthand notation of Glu-Cys-Gly.

POLYPEPTIDES

FIGURE 10.2.7 'Milking' snake venom. The components of snake venom have several medical uses and are the subject of ongoing research.

The condensation reactions between amino acids can continue to form peptide chains longer than a tripeptide. Linear chains of between 20 and 50 amino acids are called polypeptides. One of the more interesting polypeptides is DNP, dendroaspis natriuretic peptide, a polypeptide chain of 38 amino acids found in the venom of the green mamba snake. DNP acts in the arteries of the victim to increase the circulation rate, thus spreading the poison faster. Pharmaceutical companies are now extracting DNP to use in the treatment of high blood pressure (Figure 10.2.7).

Proteins

A polypeptide constructed from more than 50 amino acids is usually called a protein. The number, type and sequence of the amino acid units in a protein is referred to as the protein's **primary structure**. Two different representations of a small segment of a protein can be seen in Figure 10.2.8. The primary structure may be represented by the three-letter abbreviations for the amino acids or by a structural formula of the protein. By convention, the sequence is written from left to right, starting from the amino group (N-terminal) of the first amino acid and ending with the carboxyl (C-terminal) of the final amino acid. There are many different proteins and they perform very important roles in living things. Figure 10.2.9 shows a representation of a larger segment of a protein.

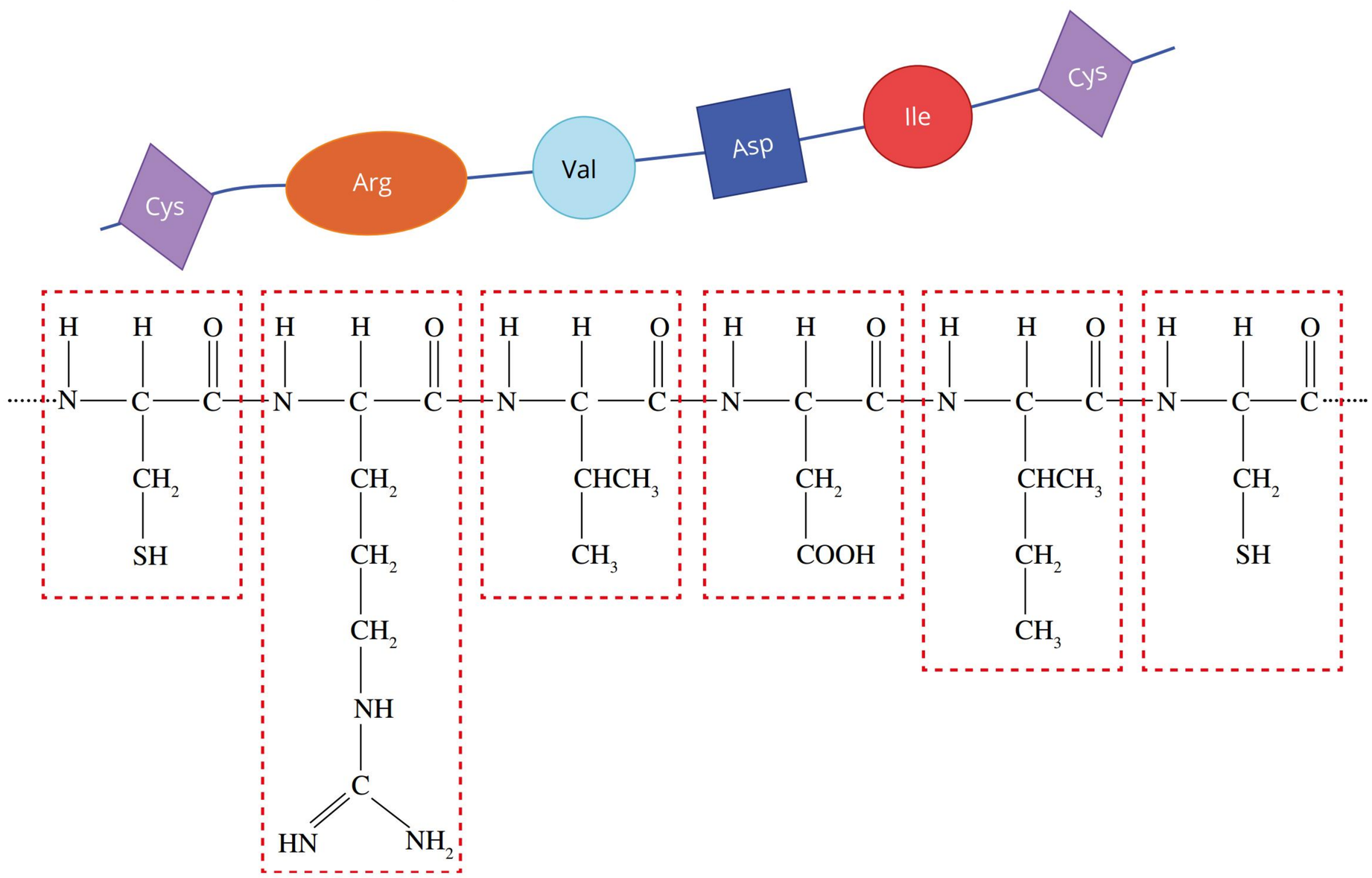


FIGURE 10.2.8 A small section of a protein molecule showing the primary structure represented by three-letter abbreviations and its structural formula. Each amino acid in the structural formula is shown in a rectangle.

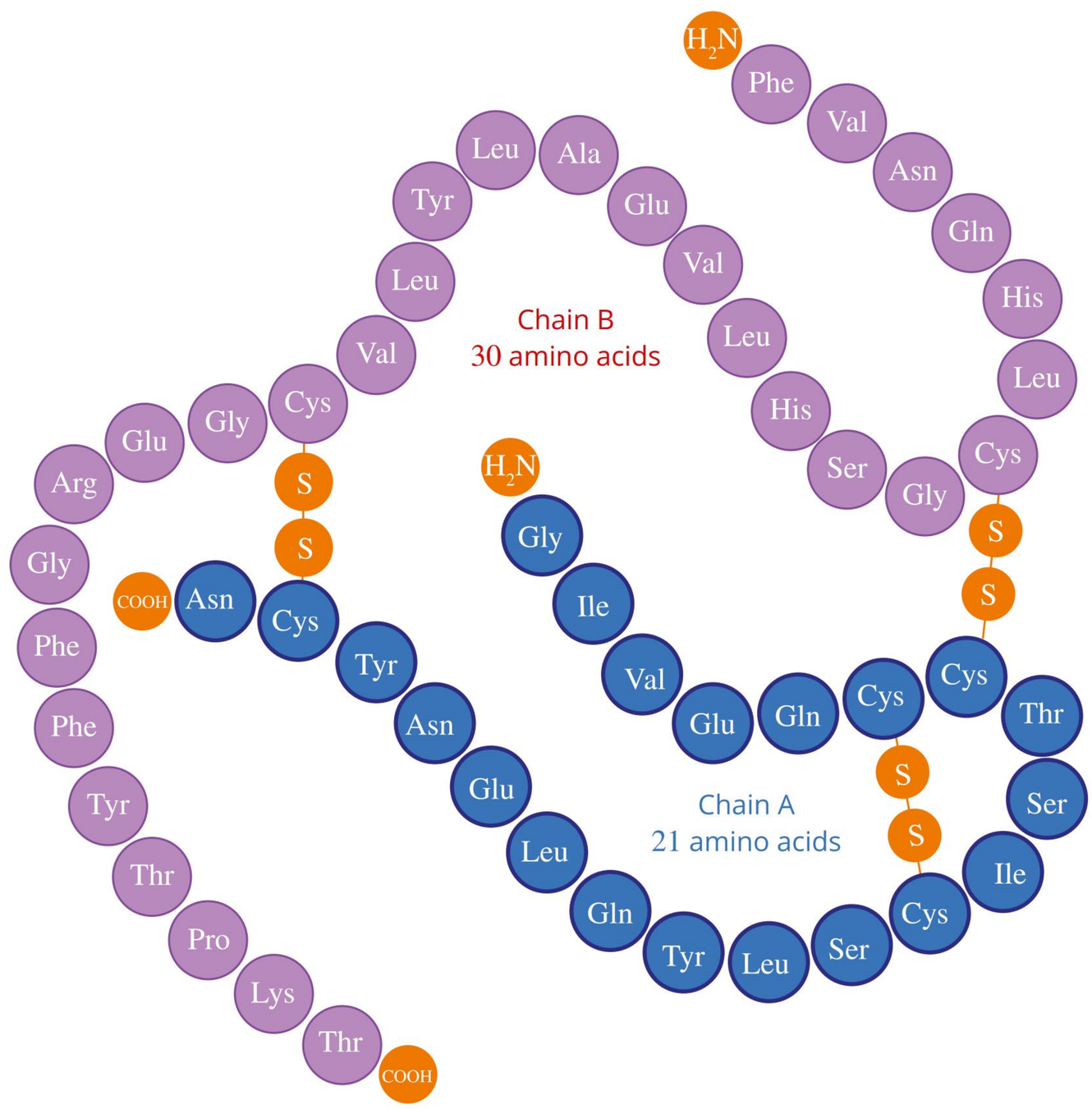


FIGURE 10.2.9 The amino acid sequence in the human insulin protein. The molecule contains 51 amino acid units.

Proteins are examples of polymers, very long molecules made from smaller repeating units. The size of a polymer molecule leads to it having significantly different properties from the monomers it is made from. When monomers join to form a polymer, the process is referred to as polymerisation. Proteins are also called polyamides, as the condensation reactions occurring between the amino acids lead to the formation of many amide links. Proteins are examples of natural polymers as they are produced in biochemical reactions. In Modules 10.3 and 10.4, you will learn about the polymerisation process in more detail.

Enzymes

One of the most important functions of many proteins in the body is as enzymes. Enzymes are biological catalysts that accelerate the rate of chemical reactions in cells. An enzyme (protein) can catalyse one reaction only; hence, the human body requires thousands of different enzymes to maintain the many important reactions occurring every second.

Figure 10.2.10 is a representation of an enzyme. The catalytic activity of an enzyme is highly specific and depends on its overall three-dimensional structure. The specific part of the enzyme molecule with which a reactant can interact is known as its **active site**. The active site is usually a uniquely shaped flexible hollow or cavity within the protein where the reaction occurs. The reactant molecule that binds with the active site is referred to as the **substrate**. The intermolecular forces are determined by the side chains of the amino acids in the peptide sequence and can include hydrogen bonds, ionic interactions, dipole–dipole attractions and dispersion forces.

One early model for the catalytic action of an enzyme is the 'lock-and-key' model. In the lock-and-key model, the substrate molecule fits into the enzyme like a key in a lock, forming an **enzyme–substrate complex**, allowing the enzyme to break the bonds in the substrate. Figure 10.2.11 shows the steps involved in an enzyme-catalysed reaction according to the lock-and-key model.

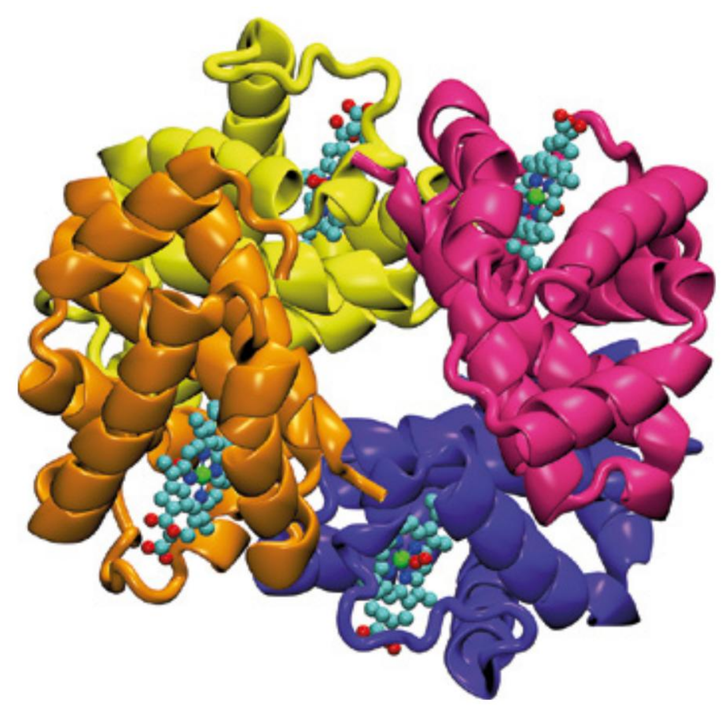


FIGURE 10.2.10 This representation of the protein haemoglobin highlights the complex and unique 3D structure of an enzyme. The active site on the enzyme allows it to bind to one particular reactant only.

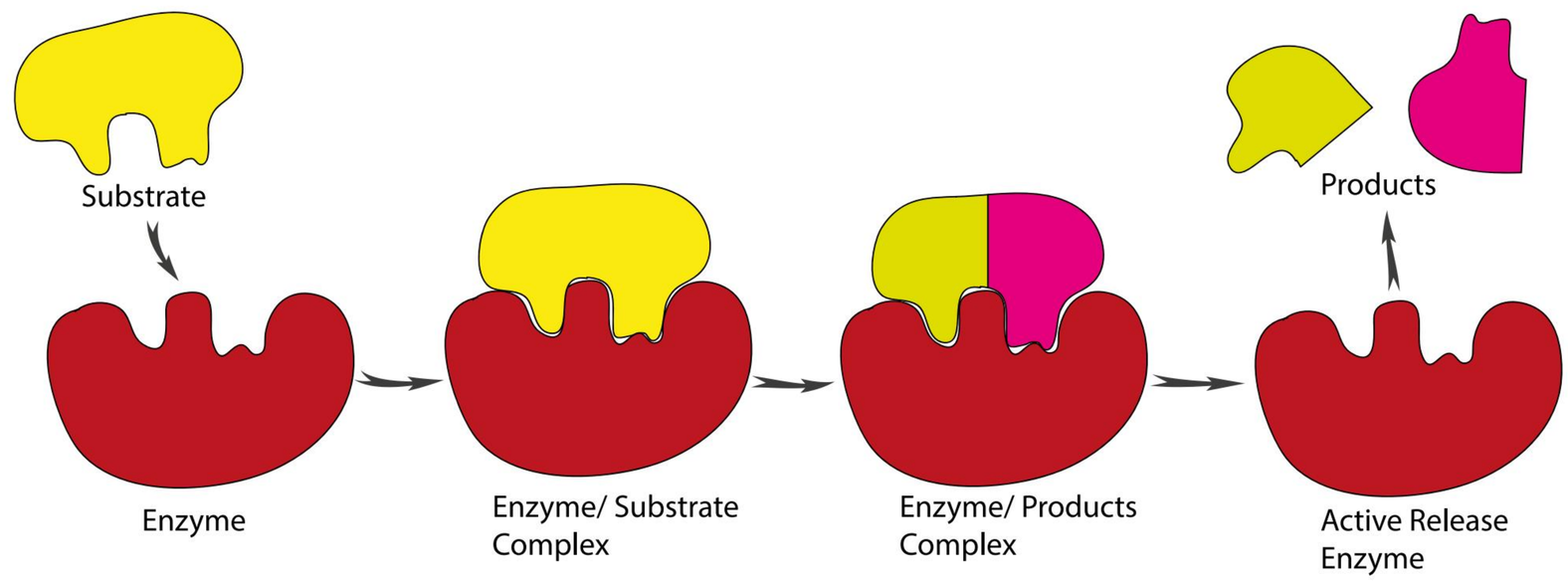


FIGURE 10.2.11 Steps in the action of an enzyme, according to the lock-and-key model

The digestion of starch is a typical example of a reaction catalysed by enzymes (Figure 10.2.12). The enzyme amylase in saliva first breaks some of the long starch molecules into smaller units, then maltase completes the breakdown, forming many glucose molecules. The breakdown of a polysaccharide into smaller saccharides is a hydrolysis reaction requiring water.

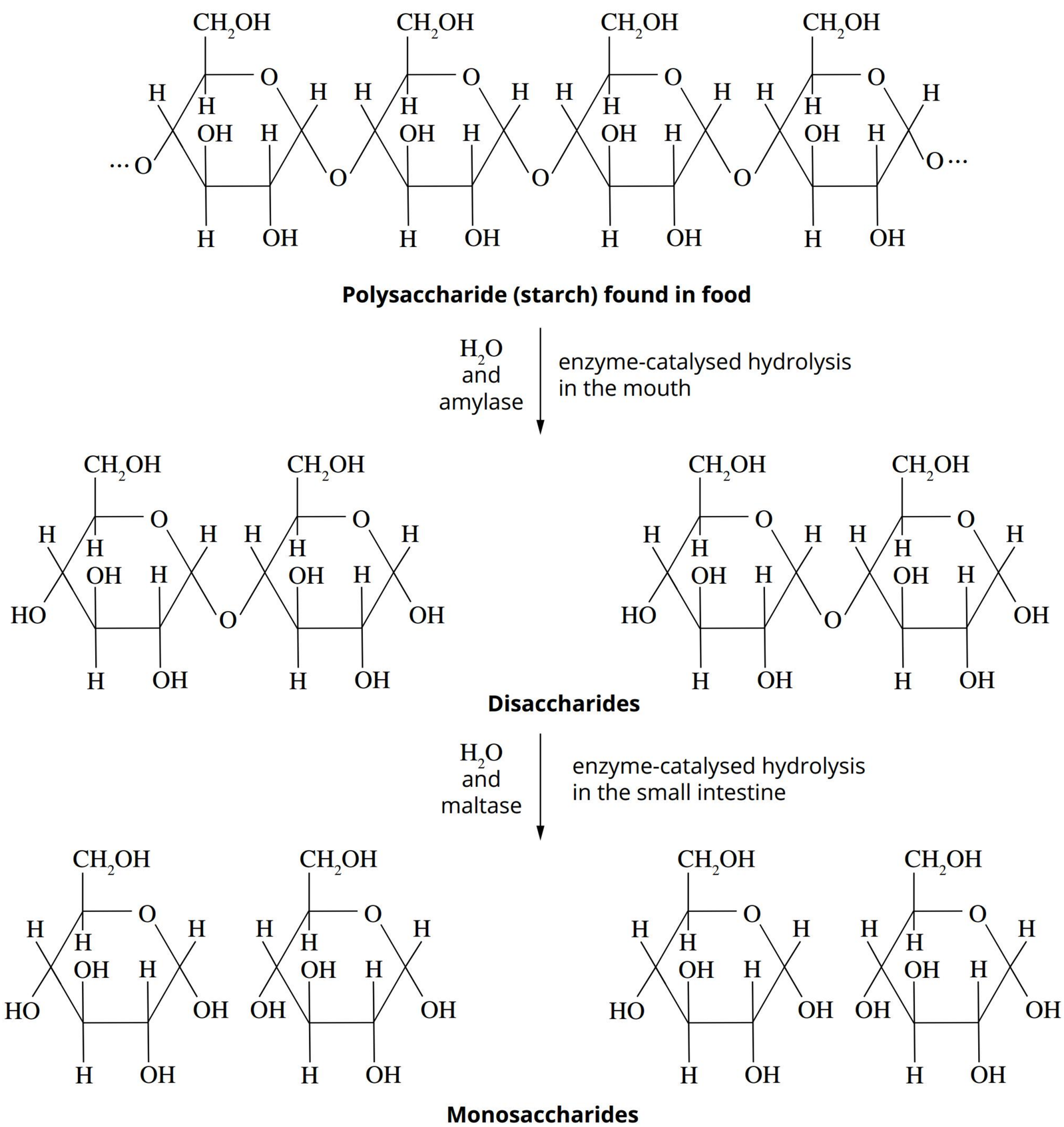
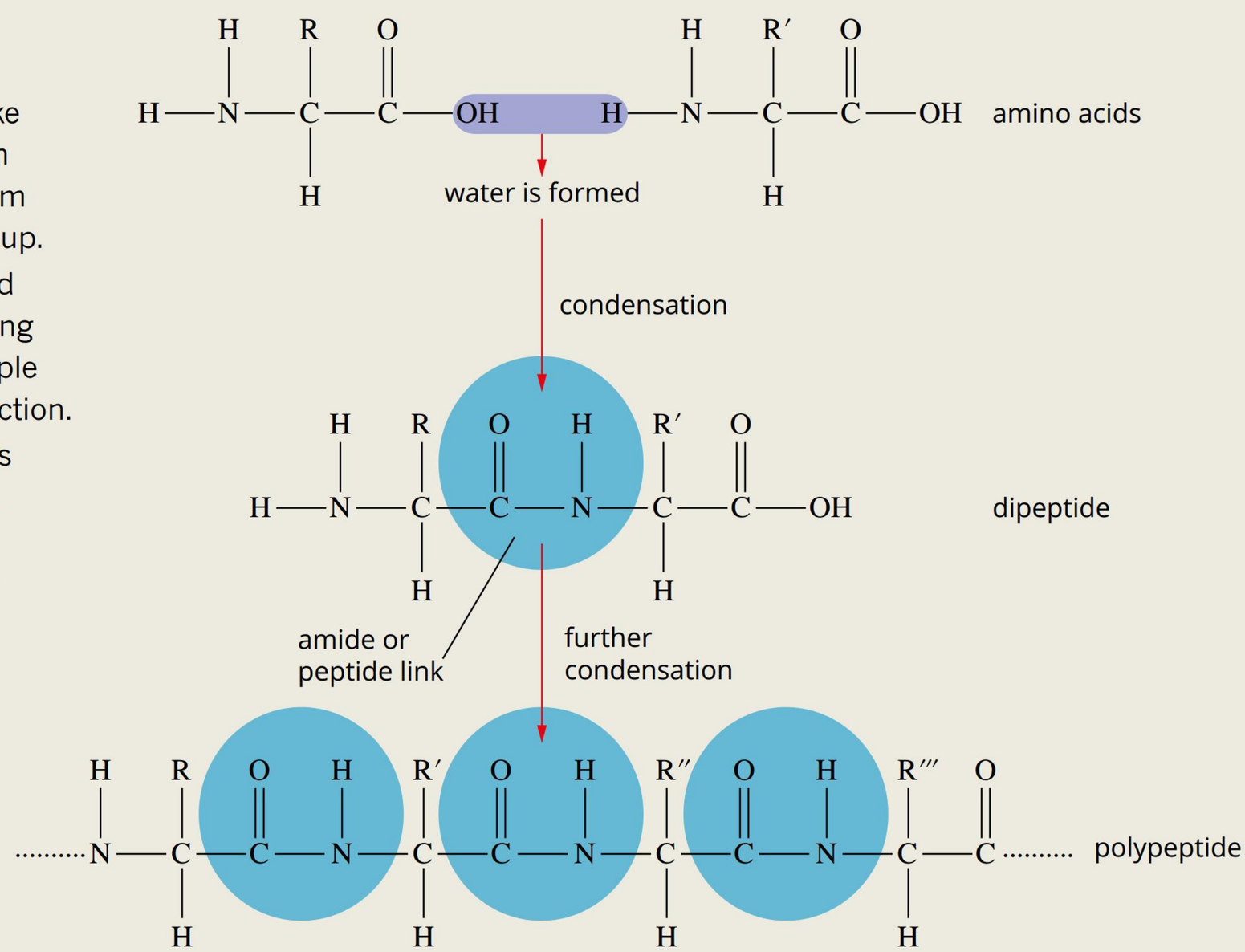


FIGURE 10.2.12 The digestion of starch is usually catalysed by two enzymes: amylase in saliva and then maltase in the small intestine.

10.2 Review

SUMMARY

- The carboxyl group and amino group of 2-amino acids can take part in a condensation reaction that links them through a peptide group.
- Water is also produced as a by-product, making this reaction an example of a condensation reaction.
- When two amino acids combine, the product is referred to as a dipeptide, while three amino acids can combine to form a tripeptide.
- In a similar manner, several amino acids combine to produce a polypeptide.
- Proteins are large polypeptide chains containing approximately 50 or more amino acids. The largest proteins have more than 30 000 amino acid residues.
- The formation of a protein is a condensation polymerisation reaction, as shown below. Condensation reactions lead to the formation of polypeptides and proteins.



KEY QUESTIONS

Describe

1 Match the terms on the left with their description on the right.

tripeptide	by-product of the reaction that produces polypeptides
R group	three amino acids joined by peptide links in a polypeptide chain
polypeptide	variable part of an amino acid
amino group	several amino acids that are joined by peptide links
water	functional group present in all amino acids

2 Describe the molecule represented by the notation Leu-Gly-Glu.

3 Complete the following table.

	Number of amino acids	Number of water molecules released	Number of peptide links formed
dipeptide			
tripeptide			
polypeptide of 38 amino acids			

Continued over page

10.2 Review *continued*

4 Choose from the terms in bold to complete the following sentences correctly:

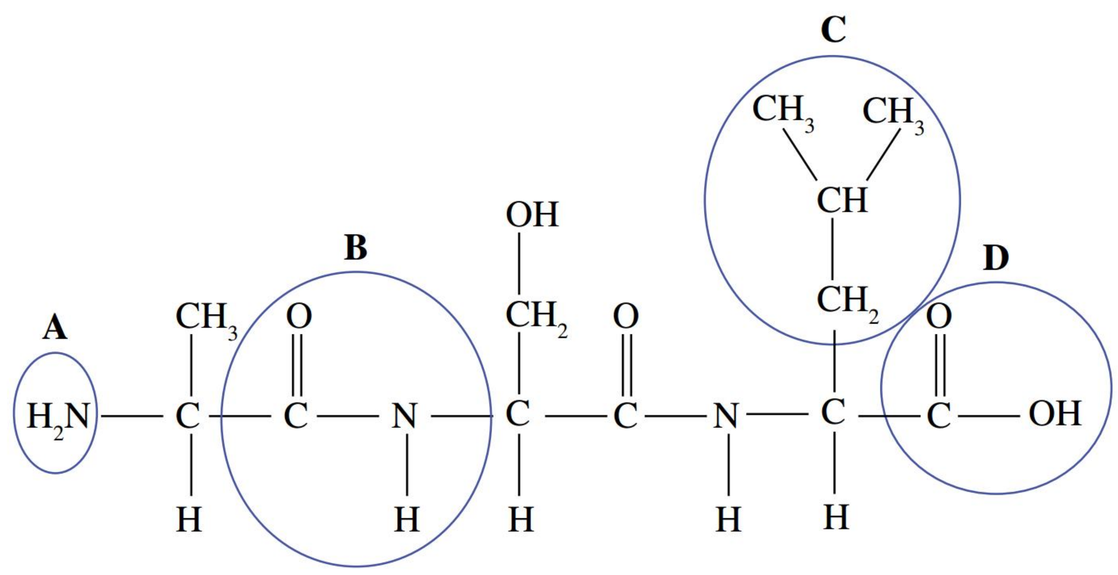
When three amino acids react together, a **dipeptide/ tripeptide/protein** is formed. The product has **one/ two/three** peptide links and **two/three** molecules of water are formed. The reaction category is **addition/ condensation**.

5 Recall what the term 'primary structure' means in reference to proteins.

6 The following figure shows a tripeptide molecule.

a Identify the parts labelled A–D.

b Referring to Table 10.1.1 on page 400, name the three amino acids in the tripeptide molecule.



Apply

7 Explain why 2-amino acids can form polypeptides.

8 Explain why proteins can also be called polyamides.

9 **a** Draw extended structural formulas of serine ($H_2NCH(CH_2OH)COOH$) and cysteine ($H_2NCH(CH_2SH)COOH$), showing all bonds.

b Write condensed structural formulas for the two possible dipeptides that could be formed from these amino acids.

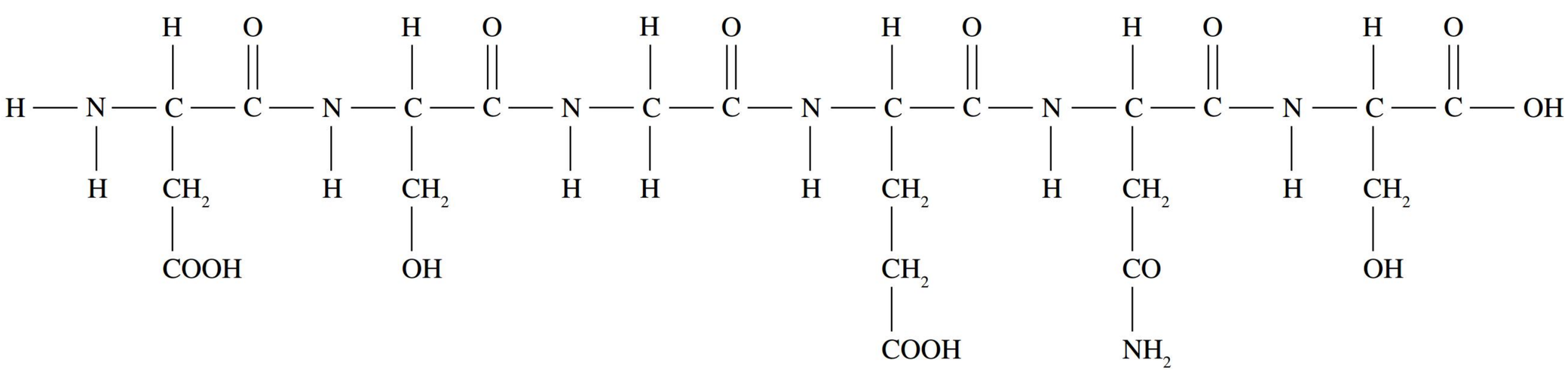
c Show the formation of one of these two dipeptides by writing an equation. Name the type of reaction used to make the dipeptide.

Analyse

10 Analyse the structure of the polypeptide, as shown in the figure below, to identify the:

a number of amino acids used to make this polypeptide

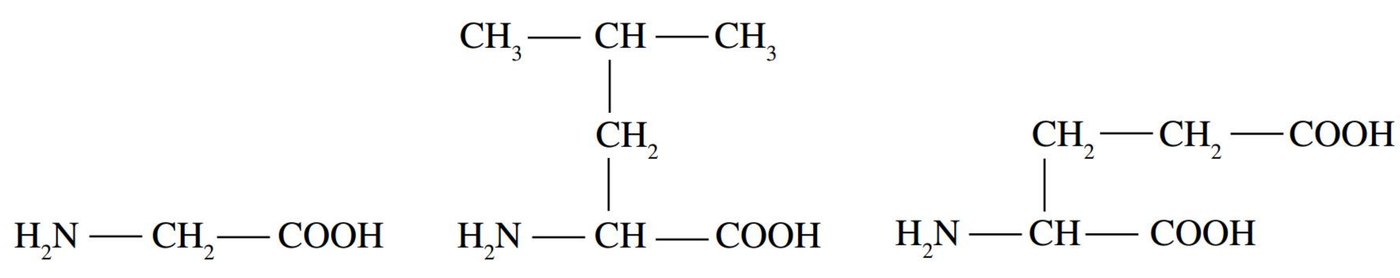
b number of water molecules produced in the reaction to make this polypeptide.



11 **a** Alanine, serine and threonine molecules react to form a tripeptide. How many different tripeptides can be formed from the three amino acids?

b Use the symbols Ala, Ser and Thr to represent each possibility.

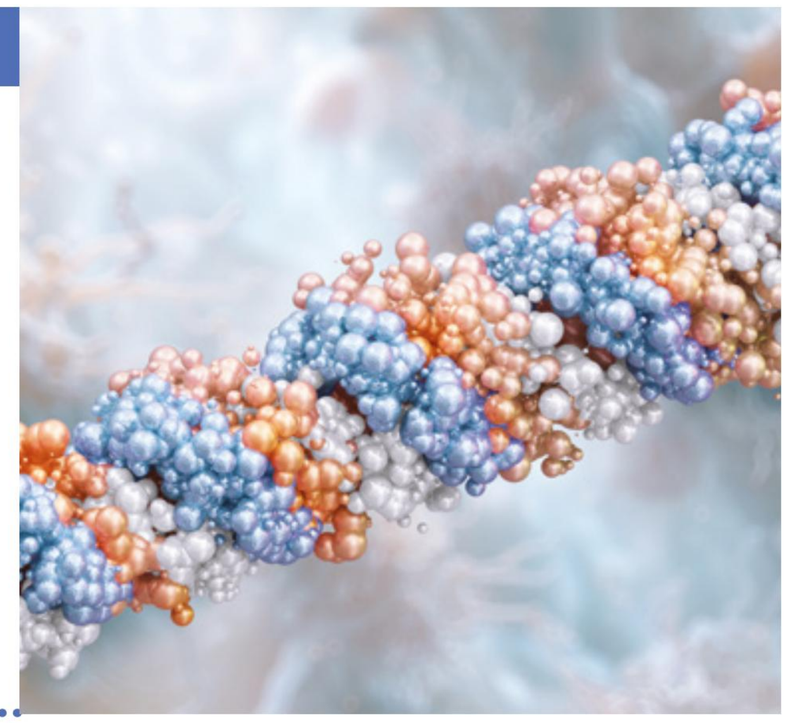
12 The three figures below show the structures for the amino acids glycine, leucine and glutamic acid. Determine why when glycine and leucine react, they can form two possible dipeptides, while when glycine and glutamic acid react, they can form three possible dipeptides.



10.3 Carbohydrates – formation and structure

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- recognise that monosaccharides contain either an aldehyde group (aldose) or a ketone group (ketose) and several –OH groups and these monosaccharides have the empirical formula CH_2O
- describe the condensation reaction of monosaccharides to form disaccharides and polysaccharides
- recognise a glycosidic bond
- understand that polysaccharides are formed when monosaccharides monomers are joined by glycosidic bonds
- distinguish between α-glucose and β-glucose
- compare and explain the structural properties of starch and cellulose.



There are millions of organic chemicals on Earth, and you do not need to look further than the plants and trees around you to find many of them. Figure 10.3.1 shows the sago palm, which is a common plant in the rainforest areas of Asia. Like many trees, the sago palm is a source of timber but, unlike most trees, its centre forms the basis of a popular dessert—sago pudding.

The main structural component of all plants, including the sago palm, is the polymer cellulose. Over half the world's organic carbon is bound up in trees and other plants in the form of cellulose.

The soft centre of the sago palm tree is a form of starch. Starch is the main component of flour, an essential ingredient of foods such as bread, cakes, sauces and pastry.

Cellulose and starch belong to a class of compounds called **carbohydrates**. In this module, you will learn about the chemical structure of common carbohydrates and their importance to nature and society.

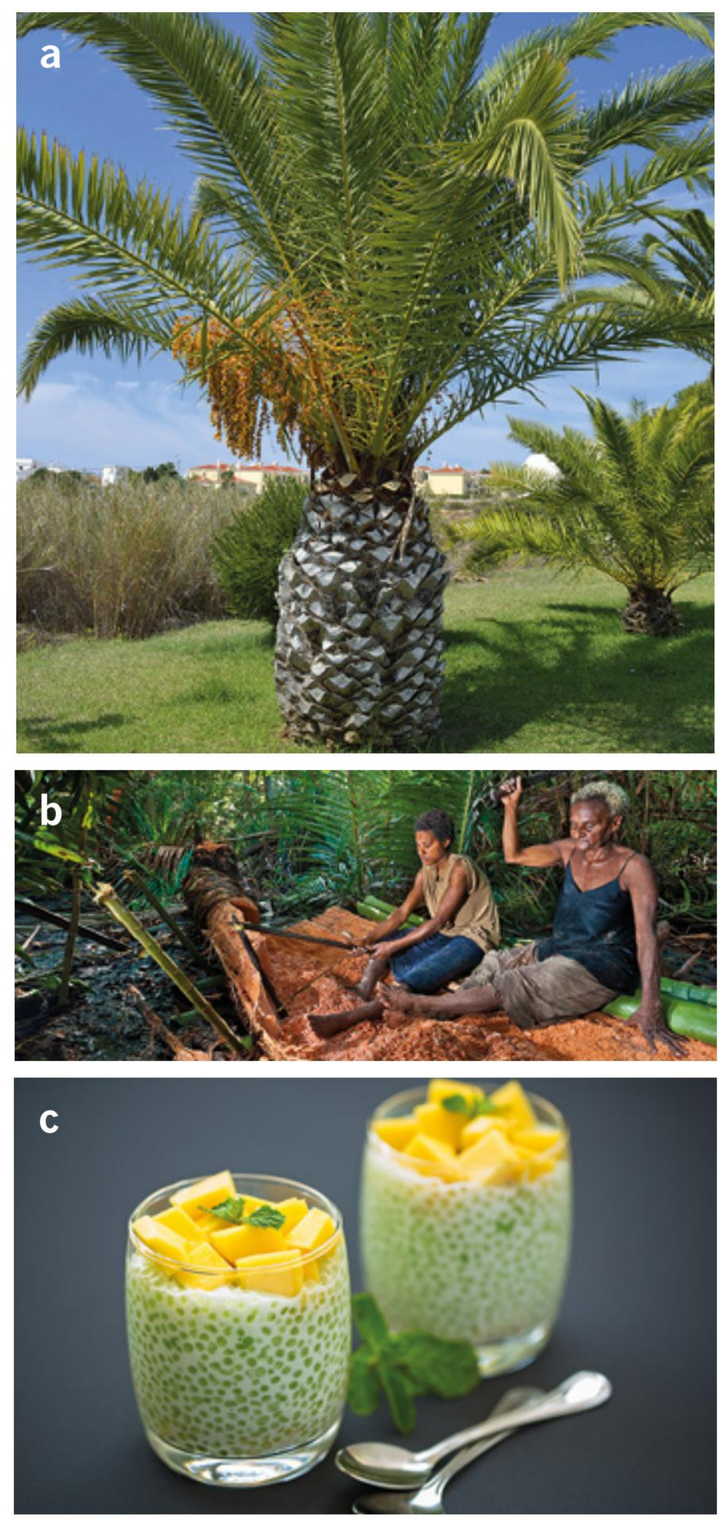


FIGURE 10.3.1 (a) The sago palm is found in rainforest areas of Asia. (b) As the sago palm ages, the centre softens and forms a product that is harvested. These women are beating the soft centre into a pulp. (c) The soft centre of the sago palm is the main ingredient in many desserts such as sago pudding.

MONOSACCHARIDES

Carbohydrates are made from the elements carbon, hydrogen and oxygen. They usually have the general formula $C_x(H_2O)_y$, where x and y are whole numbers. Carbohydrates range in size from small molecules, with relative molecular masses between 100 and 200, to very large polymers, with molecular masses greater than one million.

One of the simplest carbohydrates, glucose ($C_6H_{12}O_6$), is formed in the cells of green plants through the process of photosynthesis. Photosynthesis takes place in the presence of light and the process can be represented by the equation:

$$6CO_2(g) + 6H_2O(l) \xrightarrow{\text{light}} C_6H_{12}O_6(aq) + 6O_2(g)$$

Photosynthesis is an **endothermic** reaction, in which the Sun's energy is transformed into chemical potential energy in glucose. Living organisms use glucose as a source of energy. Animals cannot perform photosynthesis, so they need to consume plants or animals in their diet to meet their energy needs.

The smallest carbohydrates are the **monosaccharides**. They are white, sweet-tasting solids that are highly soluble in water. The structures of the three most common monosaccharides, glucose, galactose and fructose, are shown in Figure 10.3.2. Note that these monosaccharides all have the same molecular formula of $C_6H_{12}O_6$, which means they are structural isomers.

The structures of the monosaccharides look very similar, particularly glucose and galactose. However, the positions of the hydroxyl (–OH) groups in glucose and galactose are different. These slight variations in structure lead to significant differences in their functions in living organisms.

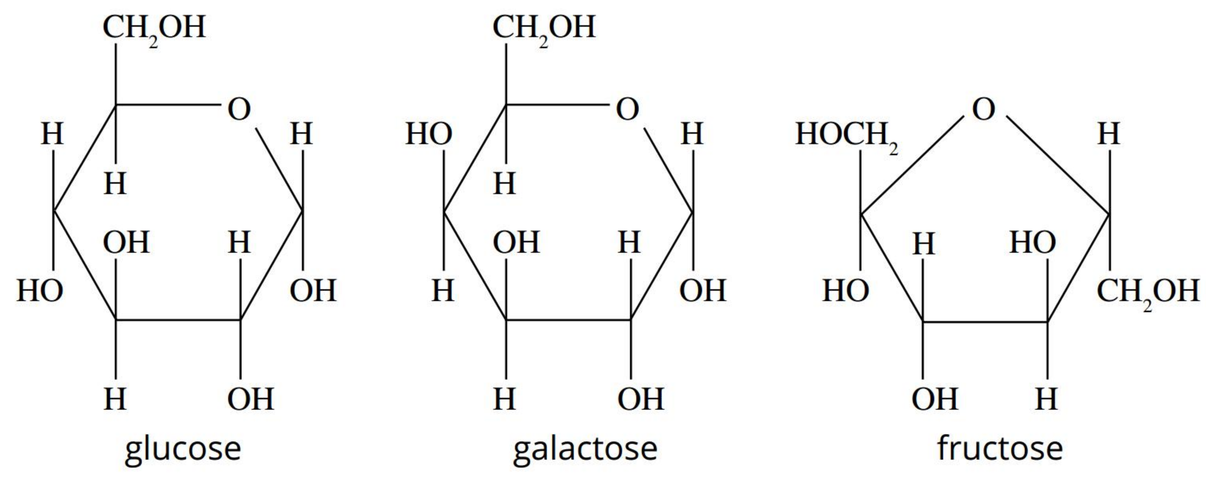


FIGURE 10.3.2 Structural formulas of glucose, galactose and fructose. Carbon atoms in the rings have been omitted for simplicity. There is a carbon atom at each corner of the ring structures except where an oxygen atom is shown.

As you learnt in Chapter 8, when there are four different groups around a carbon atom, the molecule has a chiral centre. Glucose and galactose have five chiral centres. Although all the atoms in these molecules are connected in the same way, the groups are arranged differently around one of the chiral centres. It is this difference that causes the molecules to behave differently in living organisms.

All three monosaccharides contain a number of polar hydroxyl groups, which means they can form hydrogen bonds with water. As a result, monosaccharides are highly soluble in water.

Glucose is found in all living things, especially in the juice of fruits, the sap of plants and the blood and tissue of animals. As a product of photosynthesis, glucose functions as a key energy source in most forms of life.

Fructose is found in many fruit juices and honey. Its main role in the body is as an energy source, where it is used in much the same way as glucose. Figure 10.3.3 shows some fruits with high fructose contents.

FIGURE 10.3.3 Fructose is the most common sugar in fruit, especially berries.

> **i** Glucose, fructose and galactose are structural isomers. They have the same molecular formula but different molecular structures. The differences in their structures appear slight but they are of great importance to living organisms.

Galactose is not found free in nature. However, it occurs as a component of larger carbohydrates such as lactose, the main sugar found in milk.

Carbohydrates in solution

The behaviour of some carbohydrates when they are dissolved in water can be quite complex. For example, monosaccharides can exist as isomers in equilibrium. Glucose isomers are shown in Figure 10.3.4.

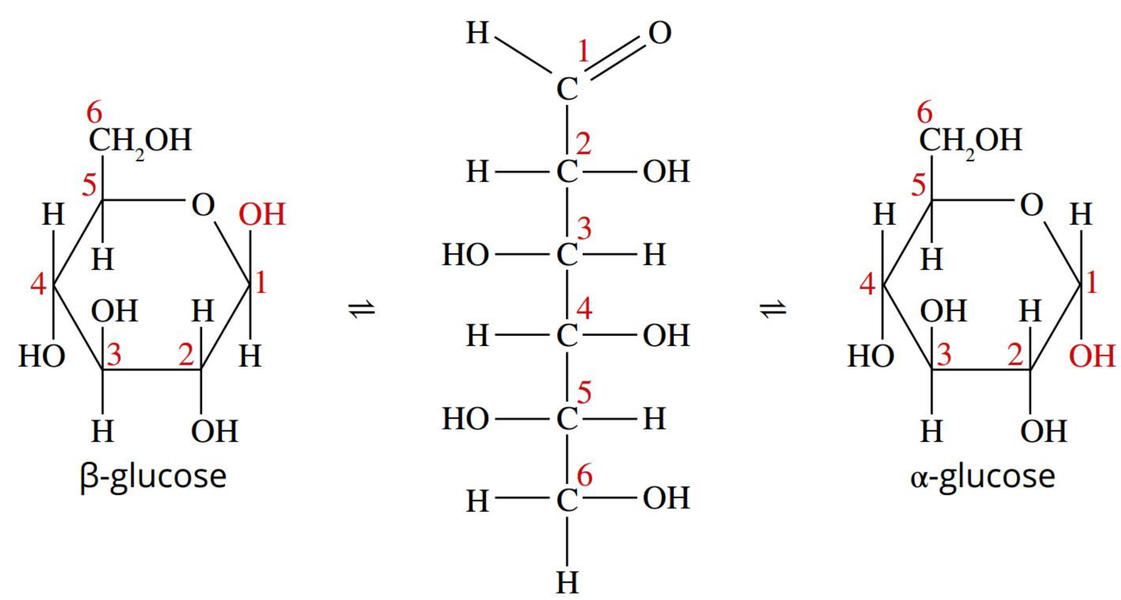


FIGURE 10.3.4 Glucose exists in solution in equilibrium between three isomers. Note the aldehyde in the straight-chain form.

The existence of these three isomers of glucose in solution allows scientists to understand why two different forms of glucose can be found in many organisms. Figure 10.3.4 shows that β-glucose can be converted to α-glucose, and vice versa, via the straight-chain form.

When the straight chain closes to make a ring, the –OH group bonded to carbon number 1 (C1) can be above the ring (in β-glucose) or below the ring (in α-glucose). At equilibrium, the majority (approximately 99%) of glucose in solution is in cyclic form, with the ratio of α-glucose to β-glucose at room temperature about 36:64. It is important to understand that α-glucose and β-glucose are different from each other. They are optical isomers, not structural isomers, as they have the same arrangement of atoms and groups of atoms, but the position of the C1 –OH group differs. A reaction between α-glucose molecules will lead to a different product from the reaction between β-glucose molecules.

In their straight-chain form, monosaccharides are classified as either **aldoses** or **ketoses** depending on their carbonyl group. The straight-chain form of glucose has an aldehyde functional group on C1, so it is classified as an aldose. The straight-chain form of fructose has a ketone functional group, so it is classified as a ketose (Figure 10.3.5).

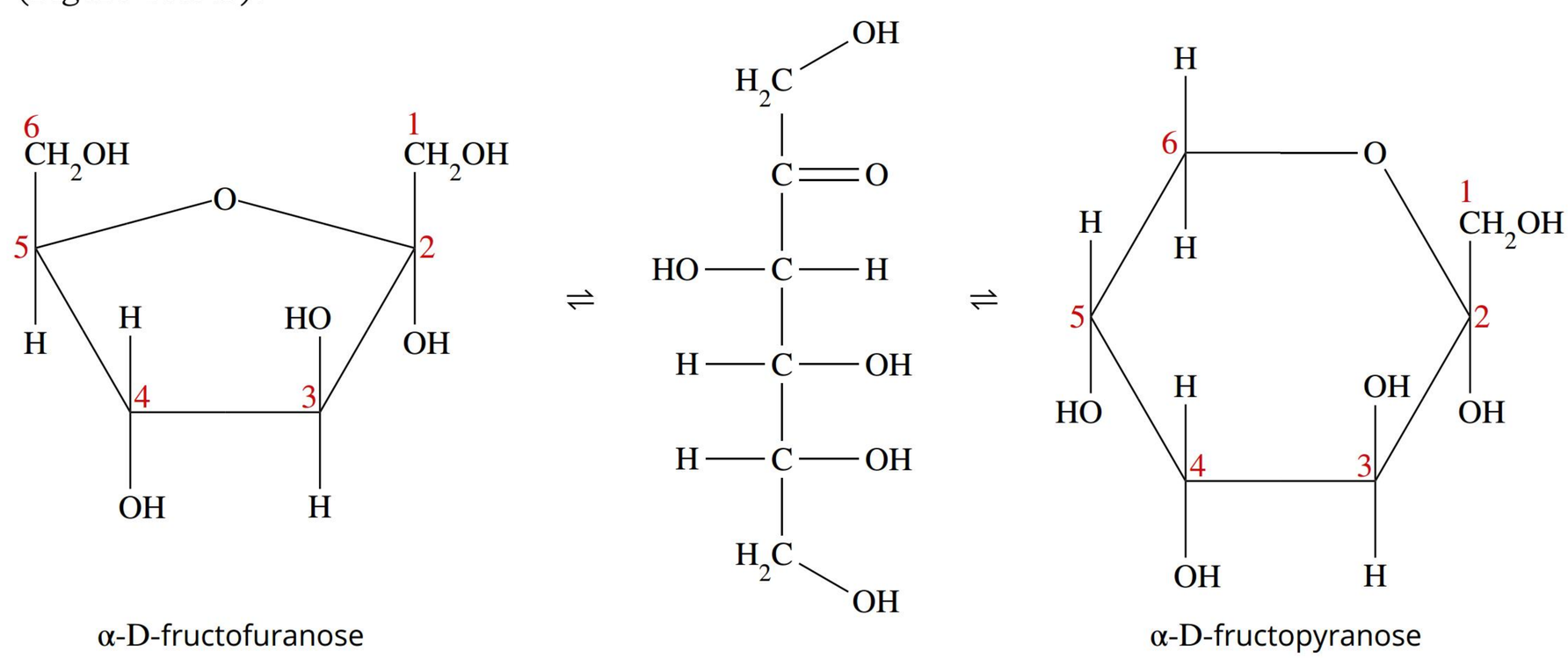


FIGURE 10.3.5 Fructose exists in solution in equilibrium between a number of isomers, three of which are shown here. Note the ketone in the straight-chain form.

DISACCHARIDES AND POLYSACCHARIDES

Two monosaccharides can join to form **disaccharides** or multiple monosaccharides can link with each other to produce a polymer, a **polysaccharide**.

Disaccharides

Disaccharides are carbohydrates formed from the reaction between two monosaccharide molecules. A condensation reaction occurs between the hydroxyl functional groups on neighbouring molecules and a water molecule is formed as a by-product.

The two monosaccharides are joined by an oxygen atom. The connection between the monosaccharide units is called an **ether bond** (or **glycosidic bond** in carbohydrates). Figure 10.3.6 shows the formation of two important disaccharides, maltose and sucrose. Note that an ether bond is not the same thing as the ester bond you learnt about in Chapters 8 and 9; the ether bond does not include a C=O, carbonyl group.

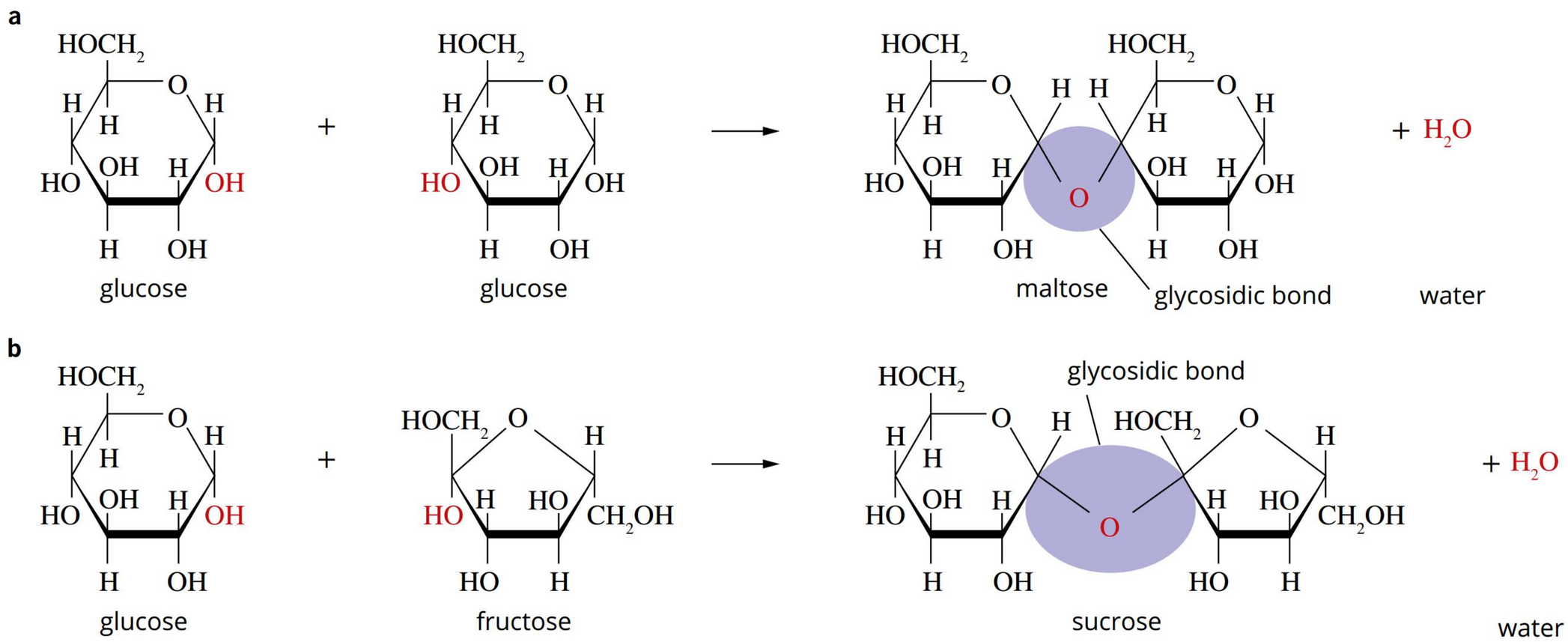


FIGURE 10.3.6 (a) The condensation of two glucose molecules forms maltose. (b) The condensation of glucose and fructose molecules forms sucrose. The glycosidic bonds are highlighted.

FIGURE 10.3.7 (a) Germinating barley seeds are a source of maltose. (b) The juice of sugar cane has a high sucrose content.

Maltose is added to foods as a sweetener and is used in the brewing industry as a raw material for fermentation into beer.

Sucrose is commonly referred to as table sugar. It is the most popular sweetener among the simple sugars. Sucrose is found in high concentrations in crops such as sugar beet and sugar cane, as shown in Figure 10.3.7.

Monosaccharides and disaccharides are often referred to as sugars because of their sweet taste. It is this sweetness that is often blamed for the dietary issues of many Australians. The lure of a sweet taste can lead people to eat more food than they require. The excess foods consumed are converted to fats, which are stored in the body.

POLYSACCHARIDES

A condensation reaction between monosaccharides does not necessarily stop with the formation of a disaccharide. Reactions with other monosaccharides can continue to produce a polymer, a polysaccharide. As glucose can exist in the two forms (Figure 10.3.8), more than one possible polysaccharide can form.

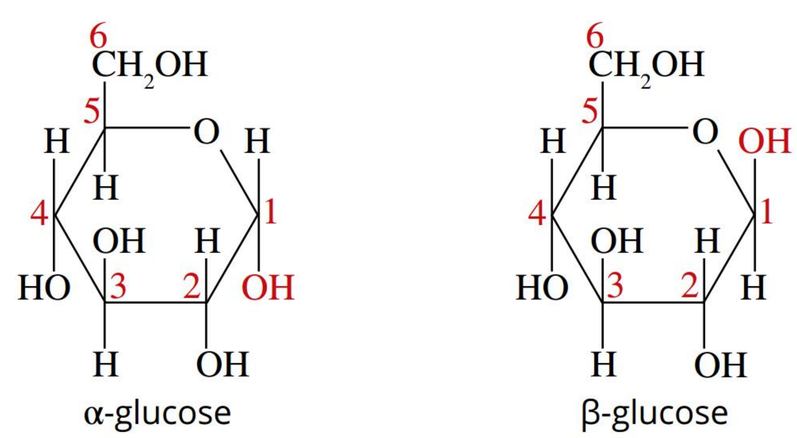


FIGURE 10.3.8 The polymerisation of α-glucose forms different products to β-glucose.

When two monosaccharides react, a disaccharide is formed. This is another example of a condensation reaction because a small molecule, such as water, is produced as a by-product. The bond formed between the two monosaccharides is called either an ether or a glycosidic bond.

Glucose can form two isomers (α-glucose and β-glucose) with different orientations of the hydroxyl group on the first carbon. It is because of these two forms that three of the most important polysaccharides found in living organisms exist—starch, cellulose and glycogen.

The three most important biological polysaccharides are starch, cellulose and glycogen. Simplified models of these polysaccharides are shown in Figure 10.3.9. Polysaccharides are generally insoluble in water and have no taste.

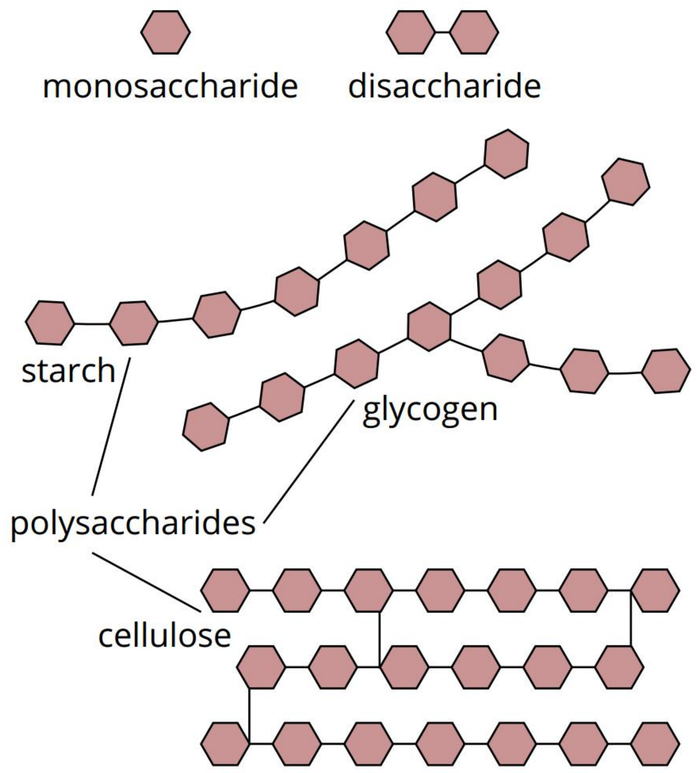


FIGURE 10.3.9 Representations of different carbohydrate molecules. The polysaccharides shown contain over 500 glucose monomers in their molecules.

Starch

Plants are able to produce and polymerise α-glucose molecules to form starch. Glycosidic bonds are formed between each glucose molecule. This also produces many water molecules as a by-product. Plants store starch so that it can later be **metabolised** to produce energy. When energy is needed, the plant can break down the starch back into glucose and react the glucose with oxygen to produce energy to maintain its functions. This reaction is respiration and can be summarised by the equation:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

Foods such as potato and sago have a high starch content. If the starch forms a linear polymer, it is known as **amylose** (Figure 10.3.10).

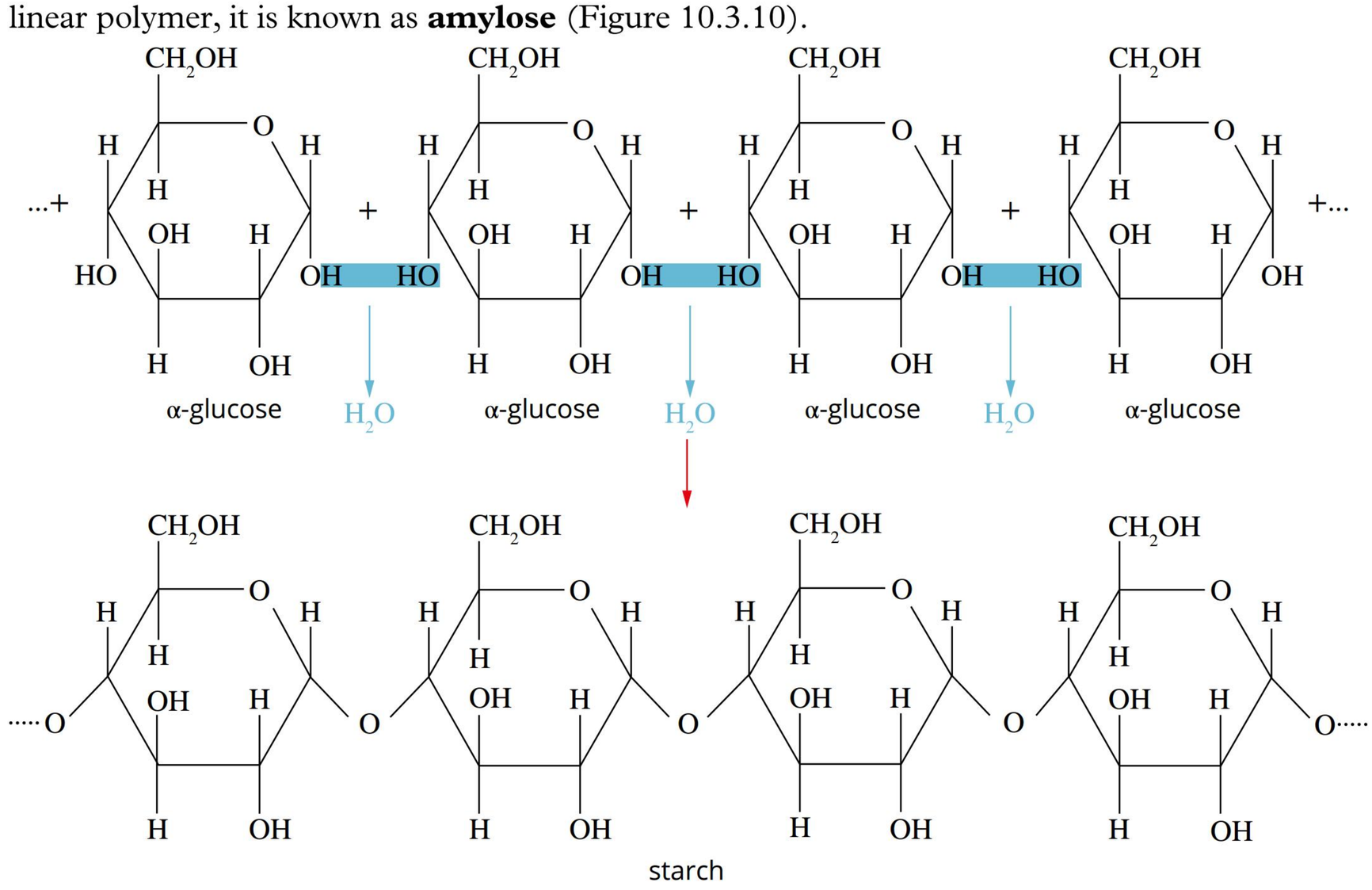


FIGURE 10.3.10 The condensation polymerisation of α-glucose to produce amylose, which is a linear form of starch

A second form of starch, known as **amylopectin**, can form if some of the α-glucose molecules undergo condensation reactions between hydroxyl groups at different positions around the glucose rings. In this way, occasional branches occur in the structure. Figure 10.3.11 shows that the branches along the polysaccharide chains occur after about 20–24 glucose units.

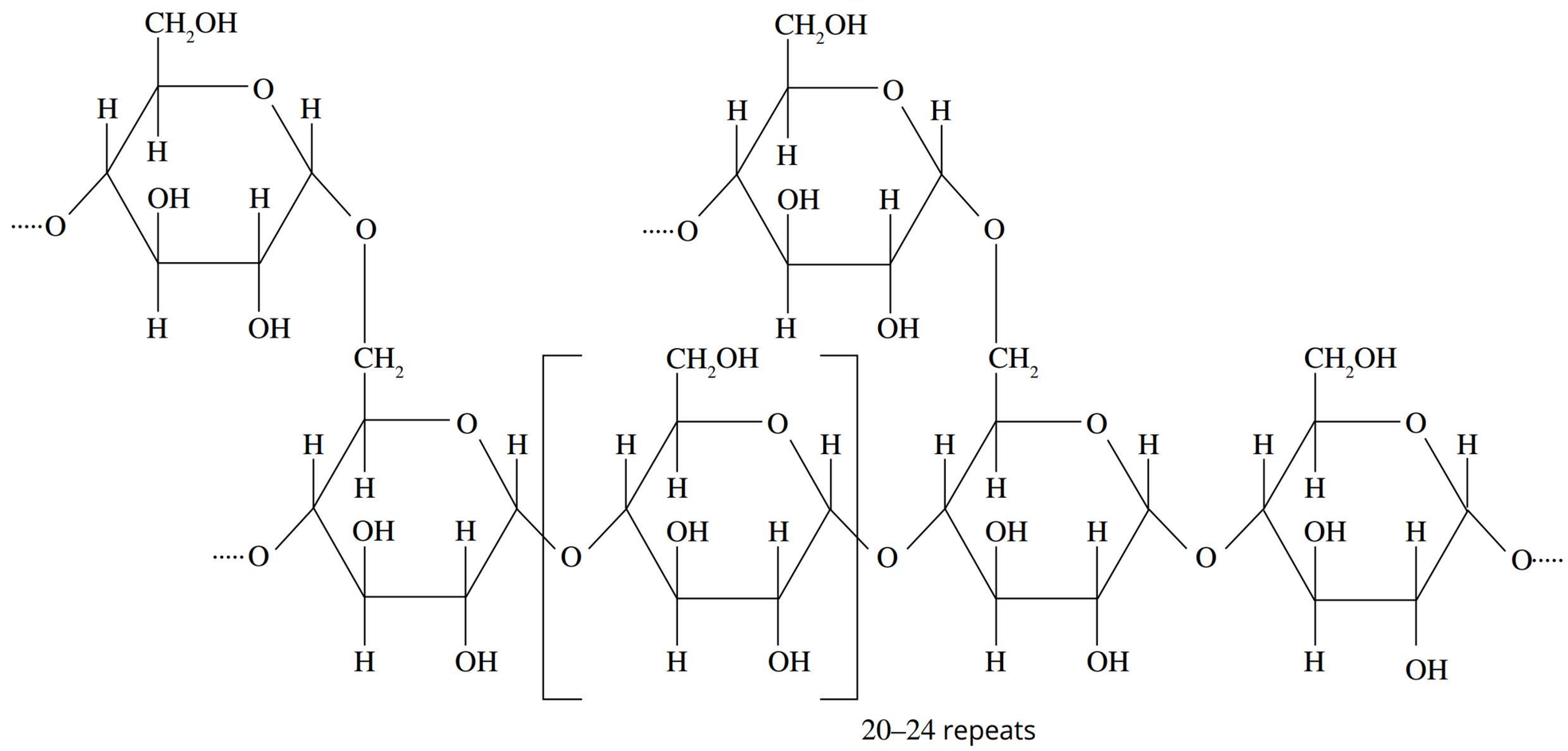


FIGURE 10.3.11 Amylopectin is a form of starch that has occasional branches along the glucose chains.

Amylose and amylopectin have different solubilities in water. The long molecules of amylose coil into spiral-like helices and pack together tightly, with many –OH groups inside the helices and away from contact with water. Therefore, amylose is largely insoluble in cold water. However, in the case of amylopectin, the branching of its molecules restricts the coiling of the polymer, leaving many more –OH groups exposed, so it is more soluble in water.

Cellulose

Cellulose is the main structural material in plants. It is the most abundant molecule in living tissue and is found in the walls of plant cells. Cotton is almost pure cellulose, while wood is around 50% cellulose. Wood also contains other polysaccharides and a significant percentage of lignin, another type of complex organic polymer.

Cellulose is a very large, straight-chain polymer formed from the polymerisation of β-glucose. The chain of glucose molecules in cellulose looks similar to that of starch. However, as Figure 10.3.12 shows, there is a different arrangement of the glucose units.

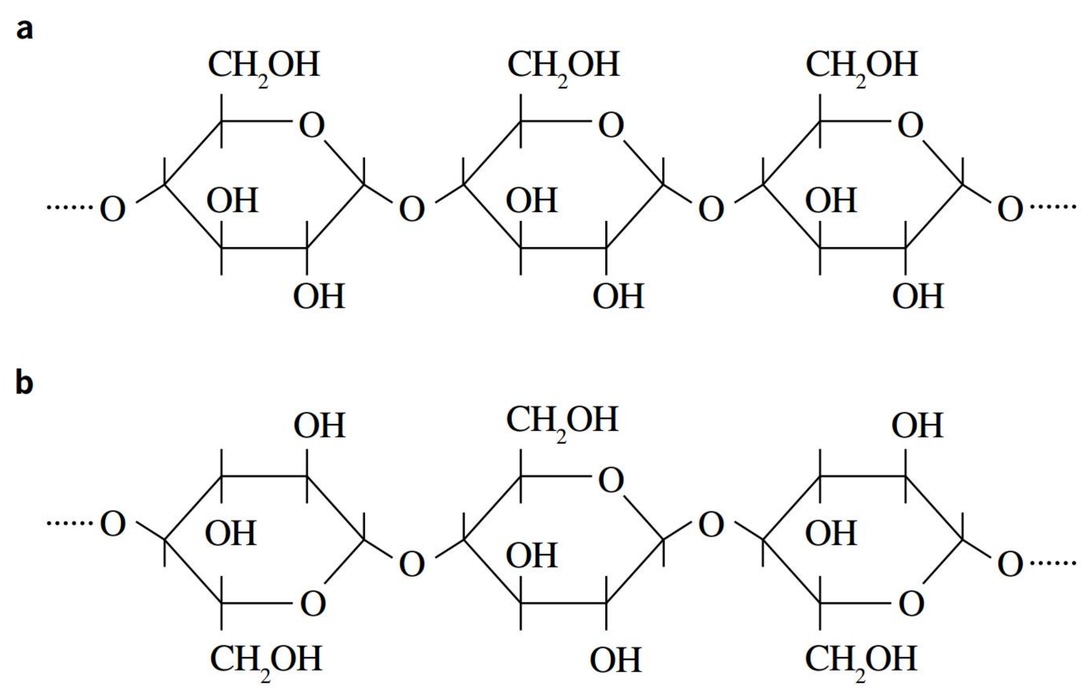


FIGURE 10.3.12 Sections of (a) starch and (b) cellulose polymers. Note the different orientations of the $-CH_2OH$ groups on adjacent glucose monomers.

Glycogen

A third polysaccharide formed from polymerisation of glucose is **glycogen**. Glycogen is a polymer of α-glucose but is highly branched in a similar fashion to amylopectin, as shown in Figure 10.3.13.

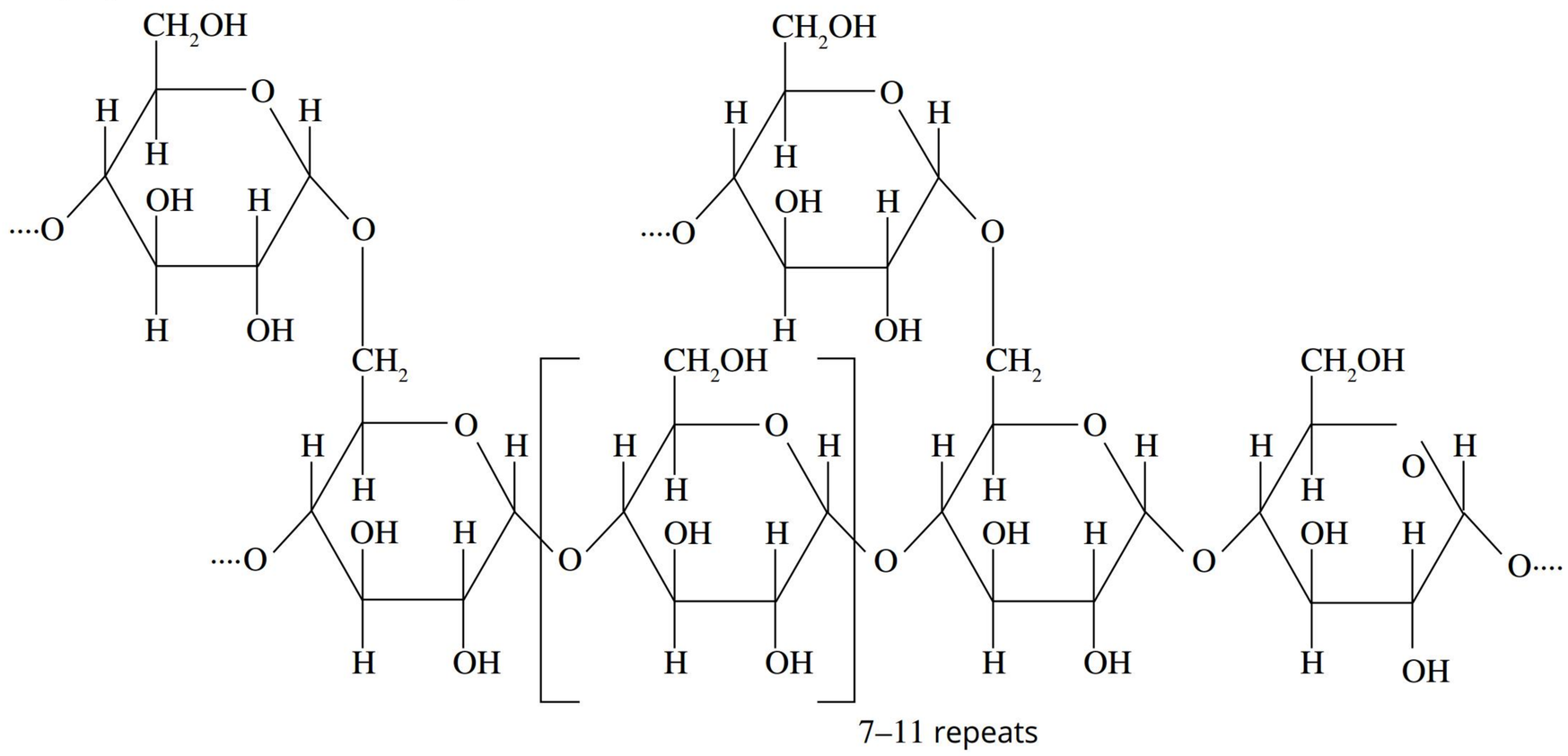


FIGURE 10.3.13 Glycogen is a highly branched polymer of α-glucose.

Animals store glycogen that will metabolise to provide energy when glucose levels are low. Glycogen is formed from excess glucose and stored in the liver or muscle tissue. If energy is needed, glycogen can be broken down into glucose, which can then be used in cellular respiration.

10.3 Review

SUMMARY

- Carbohydrates are made from the elements carbon, hydrogen and oxygen and usually have the formula $C_x(H_2O)_y$, where *x* and *y* are whole numbers.
- The main role of carbohydrates is as a source of energy for living things. Energy from the Sun is transformed to chemical potential energy in carbohydrates.
- The smallest carbohydrates are monosaccharides.
- Glucose is an important monosaccharide. It is synthesised in plants through the process of photosynthesis.
- Monosaccharides are highly soluble in water as they contain several polar hydroxyl groups, allowing them to form hydrogen bonds with water molecules.
- Disaccharides are formed from condensation reactions between two monosaccharide molecules. The bonds formed between monosaccharides are known as ether or glycosidic bonds.
- Monosaccharides and disaccharides are often referred to as sugars because of their sweet taste.
- Glucose can undergo condensation reactions to form a range of important polymers known as polysaccharides. The polysaccharides have different properties due to the different orientations of the hydroxyl groups on the glucose units and the extent of branching in the polymer chain.
- Cellulose is a structural material in plants, starch is stored in plants and glycogen is stored in animals for later metabolism into energy.

Continued over page

10.3 Review *continued*

- Important carbohydrates are listed in Table 10.3.1.

TABLE 10.3.1 Composition and source of important carbohydrates

Carbohydrate		Composition	Source
monosaccharides	glucose	$C_6H_{12}O_6$	fruit juices
	fructose	$C_6H_{12}O_6$	fruit juices, honey
	galactose	$C_6H_{12}O_6$	not found naturally in its free form
disaccharides	maltose	formed from glucose + glucose	germinating grain
	sucrose	formed from glucose + fructose	sugar cane, sugar beet
	lactose	formed from glucose + galactose	milk
polysaccharides	glycogen	polymer of α-glucose	stored in animals in the liver and muscles to be metabolised for energy
	starch	polymer of α-glucose	stored in plants to be metabolised for energy—abundant in wheat, corn, potatoes, etc.
	cellulose	polymer of β-glucose	plant fibre—in plant cell walls

KEY QUESTIONS

Describe

1 Select the correct statements about starch. (Hint: there may be more than one answer.)

A Starch is a disaccharide.
B Starch is a polymer of sucrose.
C There are two common forms of starch.
D Starch is an energy storage molecule in plants.
E Starch is composed of relatively large molecules.
F Many glycosidic bonds are formed when glucose reacts to form starch.
G All forms of starch are highly soluble in water owing to the large number of hydroxyl groups.

2 Select the correct words in bold print to complete the following sentences:
A **disaccharide/polysaccharide** is formed from the reaction between two monosaccharides. The **addition/condensation** reaction forms a **peptide/glycosidic** bond, also known as an **amide/ester/ether** bond. **Carbon dioxide/Water** is also formed in the reaction.

3 Classify each of the following carbohydrates as monosaccharide, disaccharide or polysaccharide:

amylose sucrose fructose cellulose
maltose glycogen glucose

4 Name the carbohydrate that is:

a a structural material in plants
b stored in animals so that it can later be metabolised to provide energy
c stored in plants so that it can later be metabolised to provide energy
d a disaccharide found in milk.

Apply

5 Glucose is formed in the cells of plants.

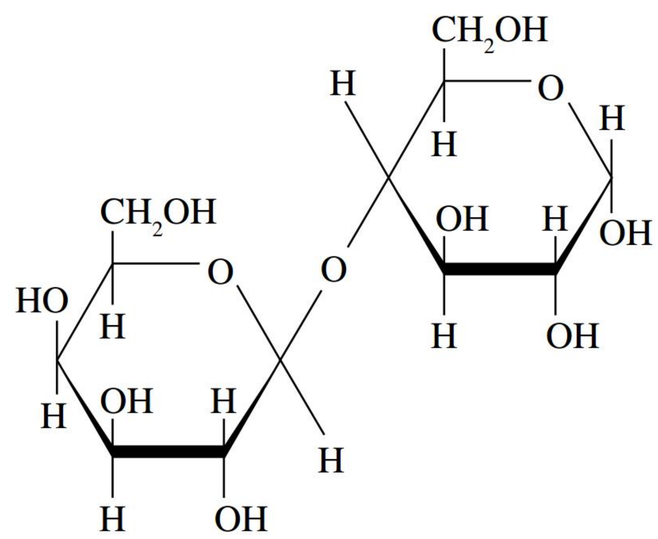
a What are the molecules that react to form glucose?
b Is the formation of glucose an endothermic or exothermic process?
c Explain how animals obtain energy from glucose.

6 Glucose is the most abundant monosaccharide. Draw a structural formula for glucose and use it to explain why it is highly soluble in water.

7 Glucose is described as a monosaccharide, maltose as a disaccharide and glycogen as a polysaccharide.

a Explain the difference between these three types of carbohydrates.
b State the type of reaction involved in converting glucose to maltose and then to glycogen.
c Identify the functional group in the molecule involved in these reactions.

8 The structure of lactose is shown below. It is formed from the reaction between glucose and one of its structural isomers, galactose.



a What category of carbohydrate does lactose belong to?

b Identify a hydroxyl group and a glycosidic bond in the molecule.

c How will the relative molecular mass of lactose compare to the combined relative molecular masses of glucose and galactose?

9 Explain the difference between α-glucose and β-glucose.

10 Raffinose is a trisaccharide found in many green vegetables. Describe three features of a raffinose molecule.

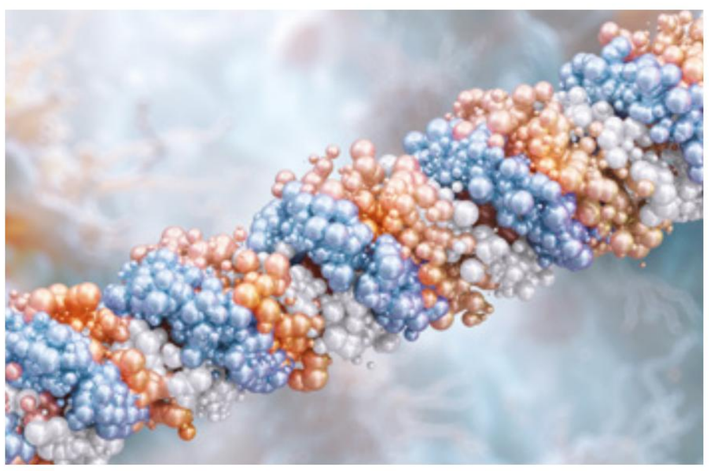
11 Cellulose and amylose are both polysaccharides formed from the same monomer glucose. Both substances perform different roles in plants. Describe the role of each.

Analyse

12 Use a Venn diagram, written paragraph, or table to identify some similarities and differences between ester bonds and ether bonds.

13 Rank the following molecules from least to most soluble in water: amylose, amylopectin, fructose and cellulose. Discuss the reasoning behind your ranking.

10.4 Synthetic polymers – formation and structure



In the previous modules, you learnt how living things can use condensation reactions to produce a variety of natural polymers such as proteins and carbohydrates. You will also learn how polymers can be produced synthetically.

You can probably identify many items that are made of polymers. Polymers are used in the construction of many different objects because they are cheap, versatile and easy to manufacture.

Figure 10.4.1 shows a range of familiar polymers. The polymers that make up these objects are selected for their properties such as strength, flexibility, durability and fire retardation.

FIGURE 10.4.1 (a) The polymer used to make the toy soccer players in this game was selected for its strength and how easy it is to mould. (b) The polymer banknotes used in Australia are strong and flexible. (c) The polymers in the helmet, gloves and bottle are similar, but differences in processing have given them very different properties.

Synthetic polymers, often just called polymers, are also referred to as **plastics**, a term frequently used to describe many items, from cling wrap to detergent bottles. For chemists, the term 'plastic' describes the property of a material, not the material itself. A substance is described as being plastic if it can be moulded into different shapes readily. This is because the material from which it is made is a plastic material.

There are thousands of different polymers, many with specialised properties. However, in general polymers are:

- light but strong. Products such as nylon rope, Kevlar yacht sails and tennis racquet frames are very strong considering the low density of the polymers used to make them.
- durable.
- versatile. Polymers are used to make a diverse range of products, from toys to the frame structure of space stations and bulletproof vests. While polymers have inherent properties, they can be changed by incorporating a range of additives to extend their uses and applications.
- acid-resistant and chemical-resistant. Most common cleaning agents, shampoos and solvents can be stored in plastic containers.
- flammable.
- thermal and electrical insulators. Consider all the appliances and electrical wiring around your house that are made up of or covered by polymeric substances. Thermal resistance is evident in pot handles, the foam core of fridges and freezers as well as in polystyrene cups.

POLYMER STRUCTURE

Polymers are covalent molecular substances composed of many small molecules all joined together. The word 'polymer' is made up of two parts, which come from Greek. *Poly* means 'many', and *mer* means 'part'. They are formed by joining

together thousands of smaller molecules, called monomers (*mono* means 'one'), through a process called **polymerisation**, as shown in Figure 10.4.2.

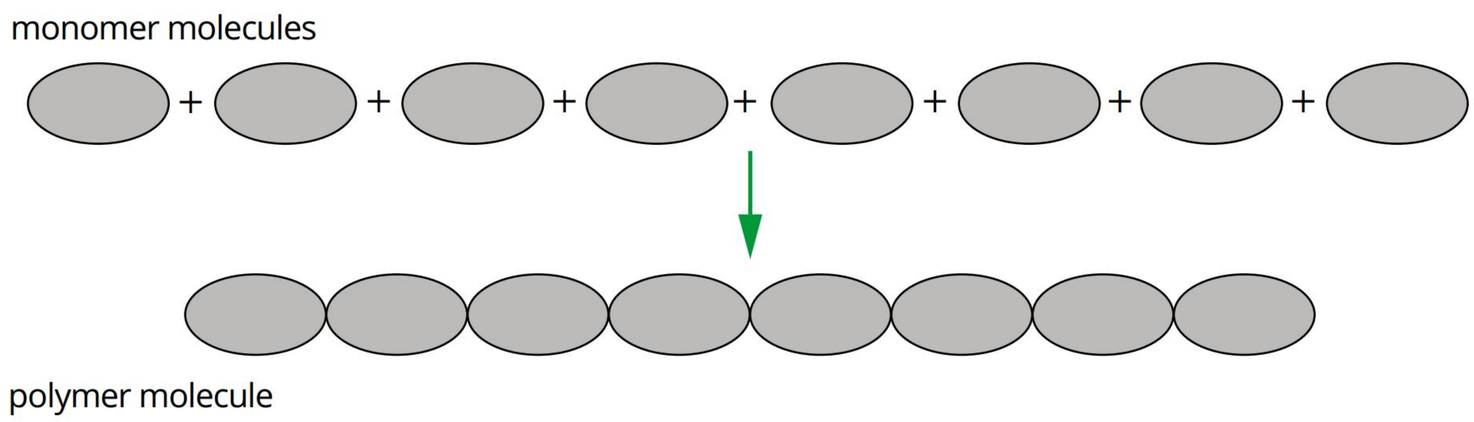


FIGURE 10.4.2 Monomers join together to form polymers.

CONDENSATION POLYMERISATION

The key feature of a monomer that makes it suitable for the formation of a condensation polymer is that it has functional groups on both ends of the molecule. Figure 10.4.3 is a reminder of the functional group reactions on an amino acid that make it possible for it to form a protein. Proteins are examples of natural condensation polymers. In this section, the structures of several important synthetic polymers are discussed.

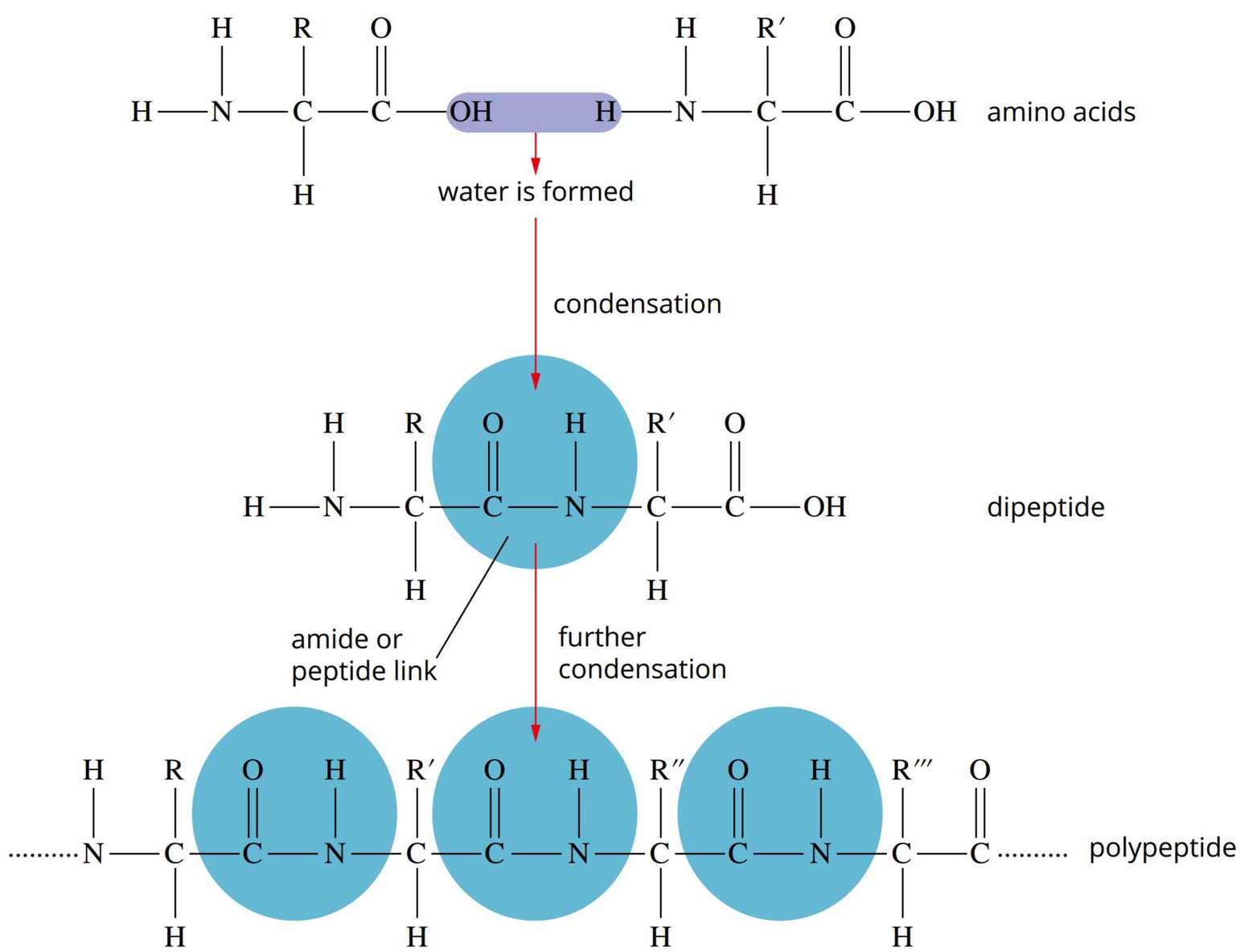
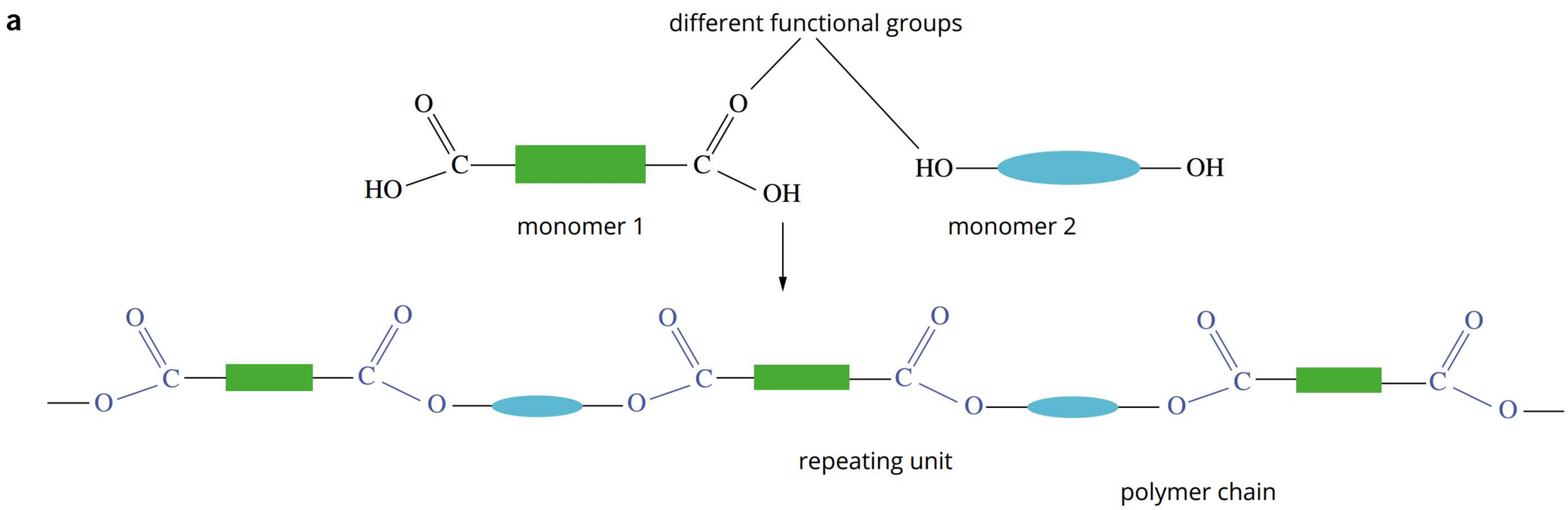


FIGURE 10.4.3 The presence of functional groups on both ends of amino acids allows many monomers to join to form a polymer. A protein is a condensation polymer made from amino acids.

Polyester

The formation of polyester is shown in a simplified way in Figure 10.4.4a. The carboxyl group on monomer 1 reacts with the hydroxyl group on monomer 2 to form what is known as an ester link. Since there are functional groups on both ends of each monomer, the same reaction can continue between further monomers to form a long polymer molecule, a polyester. Water is also formed, hence the name condensation polymerisation. Figure 10.4.4b shows the condensation reaction between each neighbouring carboxyl and hydroxyl functional groups in greater detail.



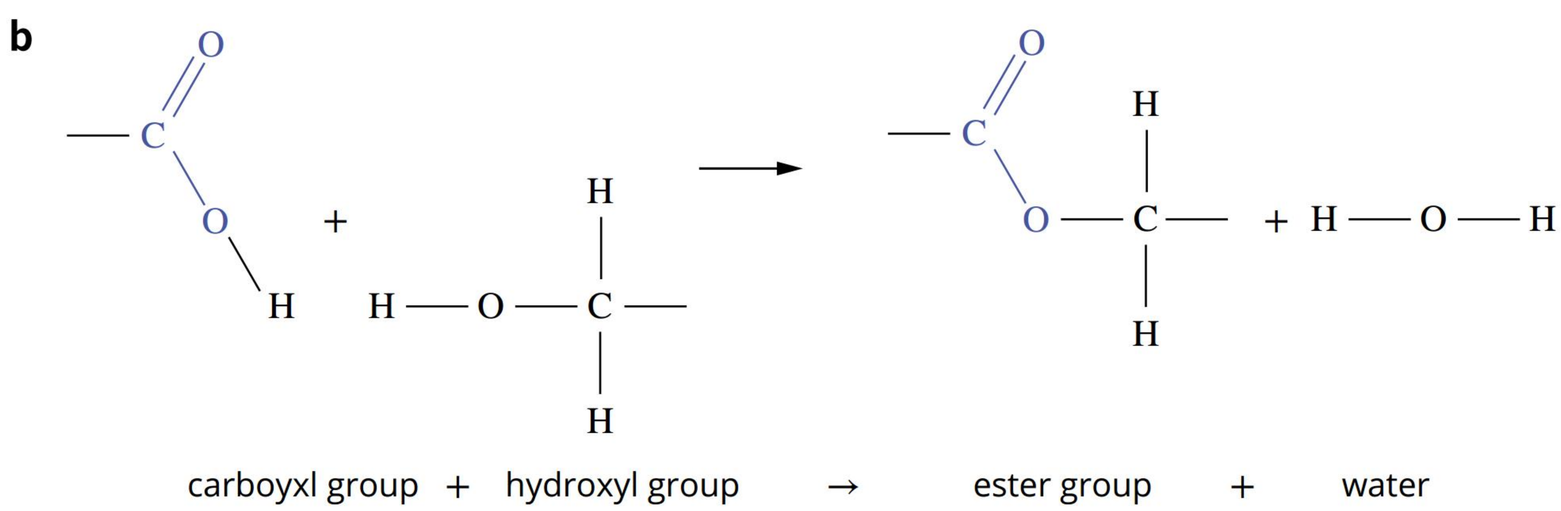


FIGURE 10.4.4 (a) Condensation polymerisation reactions require that the monomers have functional groups at each end of the molecule. These functional groups react together to form the polymer chain. (b) A condensation reaction occurs each time two monomers combine. An ester group is formed from each reaction between a carboxyl and a hydroxyl group.

The term polyester refers to a category of condensation polymers where the monomers are joined by ester links. The structure of the monomers can vary. Figure 10.4.5 shows the structure of one of the world's most used polyesters, PET (polyethene terephthalate). Note the presence of either a carboxyl or hydroxyl functional group on each end of both monomers. Polyester is described as a **copolymer** as it is formed from a reaction between two different monomers. PET might be familiar to you as polyester fabric (Figure 10.4.6a) or bottled water containers (Figure 10.4.6b). Any plastic item with recycling code 1, as shown in Figure 10.4.6c, is made from PET.

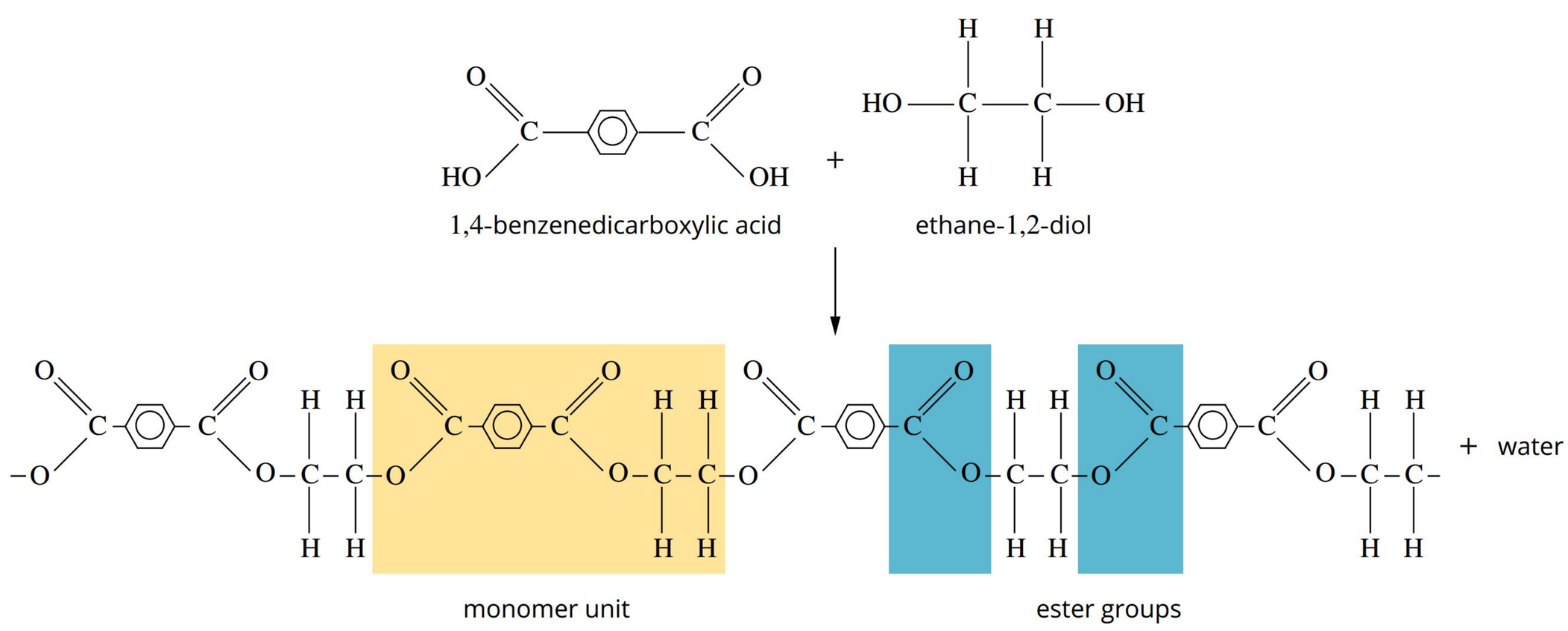


FIGURE 10.4.5 Polyethene terephthalate (PET) is formed when benzene-1,4-dioic acid reacts with ethane-1,2-diol. The PET is linked by ester groups, which is why it is part of the polyester family of polymers.

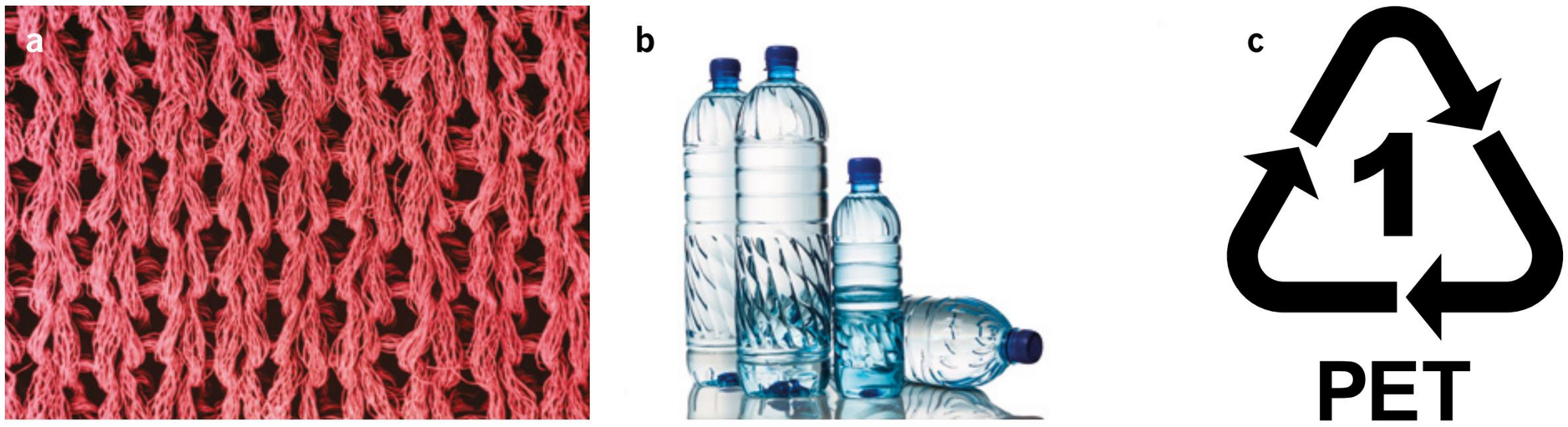


FIGURE 10.4.6 Polyethene terephthalate (PET) has many uses. (a) A microscope view of knitted polyester fibres used in clothing. (b) PET is commonly used to make plastic bottles. (c) The recycling code for bottles and other items made of PET is 1.

Polylactic acid

The formation of a condensation polymer does not necessarily require two different monomers. When polylactic acid is formed, the only monomer required is lactic acid. It has a different functional group on each end of the monomer. This polymerisation reaction is shown in Figure 10.4.7.

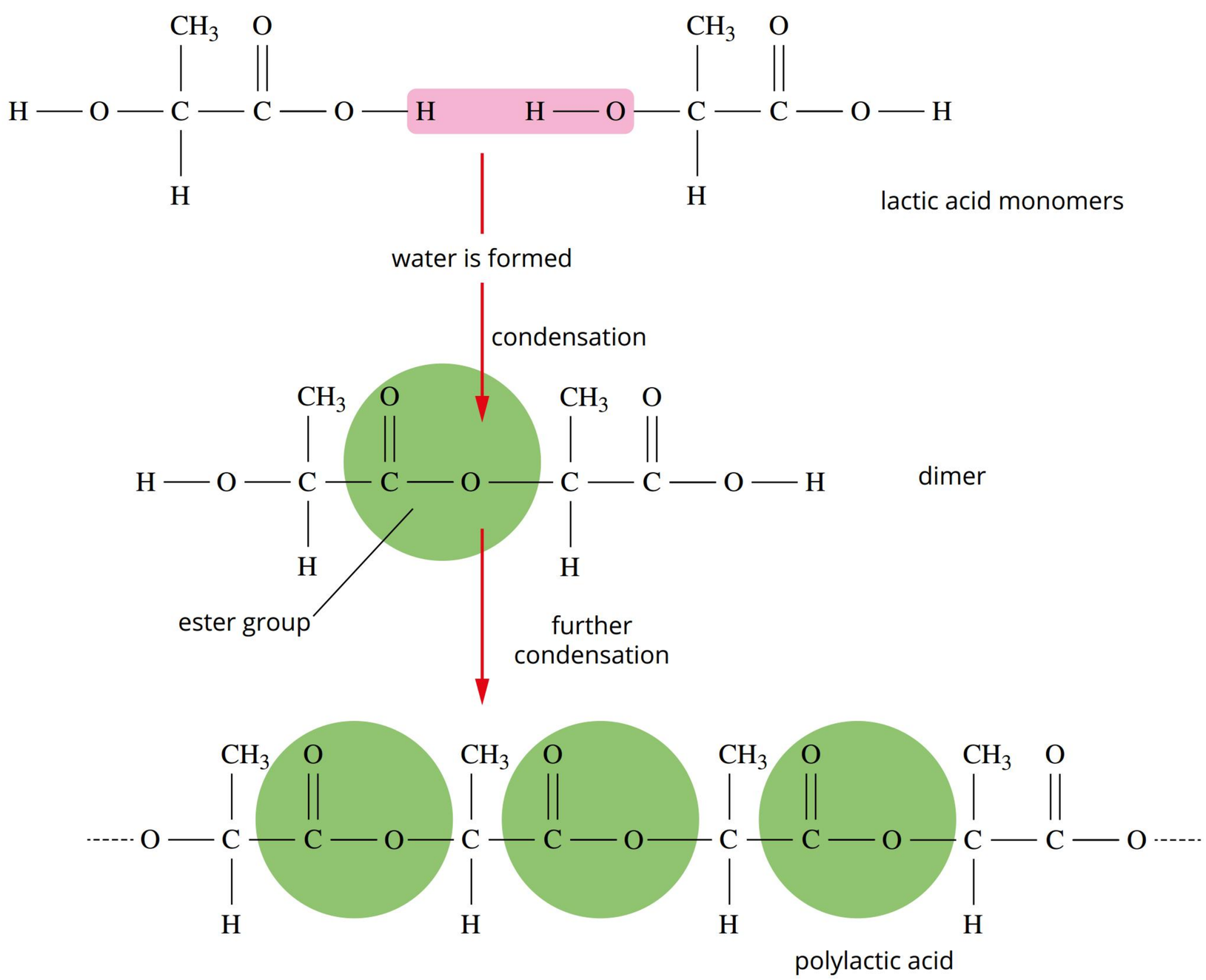


FIGURE 10.4.7 Polylactic acid is a condensation polymer made from one kind of monomer. Water is also formed.

Polylactic acid (PLA) is becoming increasingly popular for plastic products due to its sustainability potential. The monomer, lactic acid, can be produced by bacteria from biomass such as waste fruit or milk and the polymer degrades readily.

Nylon

In a similar way to the formation of polyesters, polyamides can be produced by the condensation of a monomer with two amino groups and a monomer with two carboxylic acid groups. An example is nylon, one form of which is shown in Figure 10.4.8.

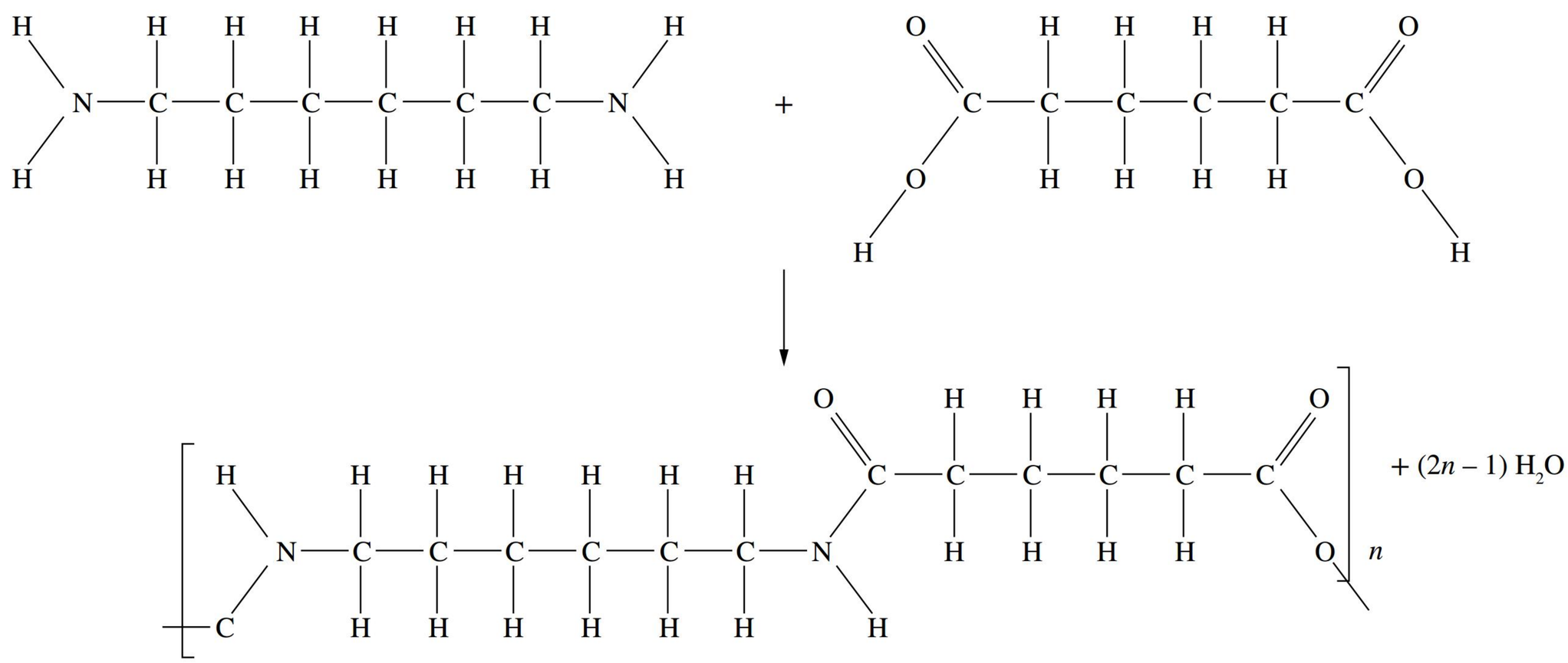


FIGURE 10.4.8 The formation of nylon by the condensation reaction between 1,6-hexanedioic acid and 1,6-diaminohexane. The term 'nylon' is given to a series of polyamides. The length of the carbon chains in the monomers can vary. A single monomer can be used if it contains an amino group on one end and a carboxyl group on the other. The diagram also shows that for a given number of monomers joining, *n*, the number of water molecules forming will be 2*n*–1.

ADDITION POLYMERISATION

You learnt in Chapter 9 that **addition reactions** involve the reaction of an alkene with another molecule. Under controlled conditions, alkenes can also undergo an addition reaction with themselves to produce long chains. This is known as addition polymerisation.

Polyethene

Ethene is an unsaturated molecule because it contains a carbon–carbon double bond. When ethene polymerises, the double bonds break and single covalent bonds are formed between carbon atoms on nearby monomers.

The reaction of the monomer ethene with itself to form polyethene, shown in Figure 10.4.9, is an example of the addition polymerisation process. Polyethene is the most commonly produced plastic in the world, being used for a range of packaging materials and containers.

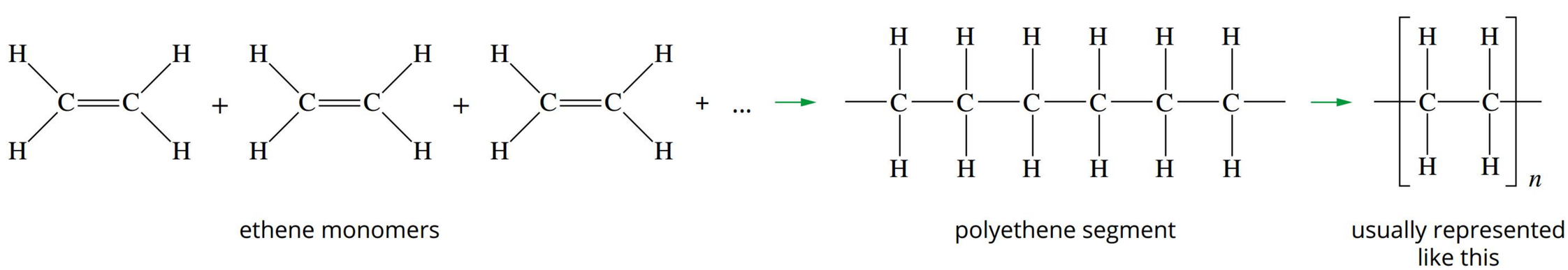


FIGURE 10.4.9 Thousands of ethene monomers join together to make one chain of polyethene. The standard notation shown simplifies the drawing of such a large chain.

Large square brackets and the subscript *n* are used to simplify the drawing of long polymer molecules. The value of *n* may vary within each polymer molecule, but the average molecular chain formed might contain as many as 20 000 carbon atoms. Polymers really are very large molecules!

Since all the atoms of the monomers are present in an **addition polymer**, the empirical formula of the monomer is the same as that of the polymer. Figure 10.4.10 provides an alternative representation of a polyethene chain segment as a ball-and-stick model.

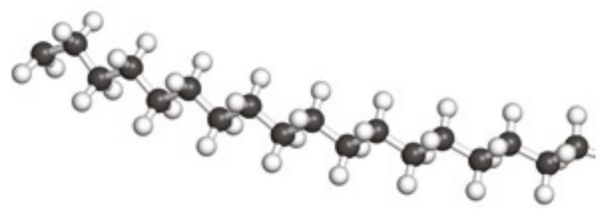


FIGURE 10.4.10 A ball-and-stick representation of a segment of polyethene

The name of a polymer formed through addition polymerisation will often include the monomer that was used to make it. The names of three common addition polymers and their monomers are listed in Table 10.4.1.

TABLE 10.4.1 Monomer and polymer names

Monomer	Polymer
ethene	polyethene
propene	polypropene
tetrafluoroethene	polytetrafluoroethene

Polypropene

Polypropene (PP) is an addition polymer made from the monomer propene ($CH_2{=}CHCH_3$), as shown in Figure 10.4.11.

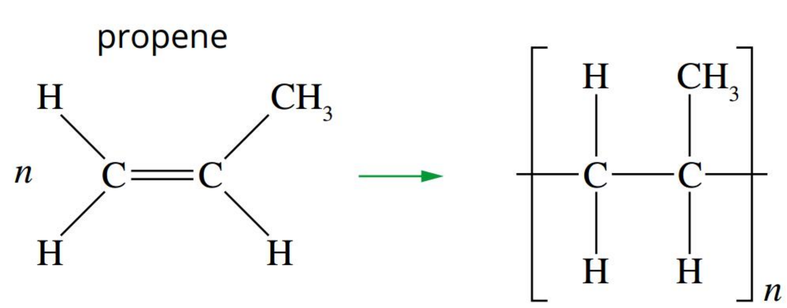


FIGURE 10.4.11 Propene undergoes addition polymerisation to form polypropene.

The way the methyl side groups ($-CH_3$) are arranged along the polymer chain has a significant effect on the properties and uses of this polymer. Figure 10.4.12 shows the three different structural forms of polypropene.

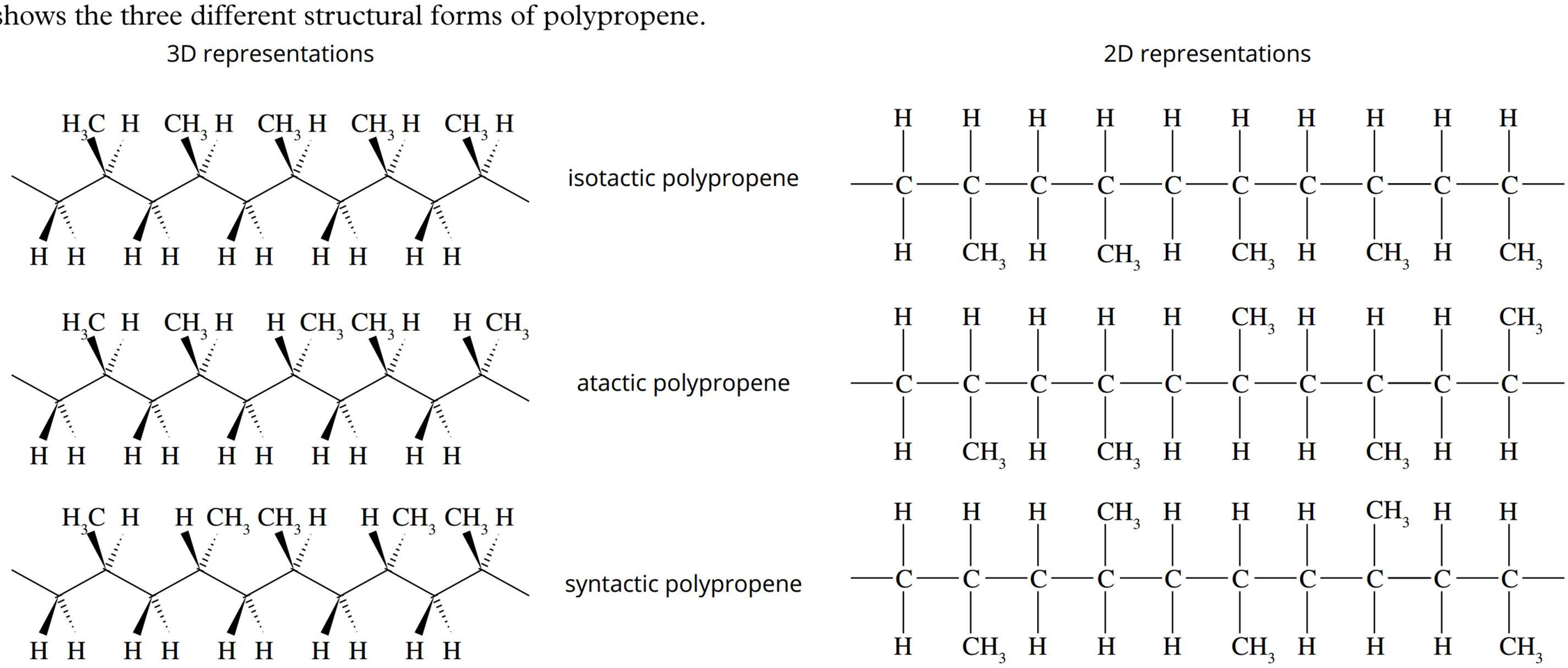


FIGURE 10.4.12 Sections of three different structural forms of polypropene

Isotactic polypropene has all the side groups on one side of the polymer chain. This allows crystalline regions to form, and significant attractive forces between the chains. This polymer material is used in many applications. For example, it is used to make babies' bottles that can be sterilised in boiling water without softening, Australian banknotes, very strong fibres and ropes, thermal underwear and polar fleece jackets.

Atactic polypropene has the side groups randomly distributed. This prevents the chains from stacking together well and forming crystalline regions. Atactic polypropene is very soft and has limited usefulness.

Syntactic polypropene has the side groups on regularly alternating sides of the polymer chain. This allows for good packing and the material is highly crystalline. It is a relatively new form of polypropylene, and many new applications are currently being explored that utilise its excellent thermal and electrical properties. It is used in place of polyethene if heat resistance or toughness is important, and it can be made into an **elastomer** like rubber. Elastomers are polymers that can stretch when pulled but return to their original shape when released.

Teflon (polytetrafluoroethene)

Tetrafluoroethene ($CF_2{=}CF_2$), shown in Figure 10.4.13, is formed when all the hydrogen atoms in ethene are replaced by highly electronegative fluorine atoms.

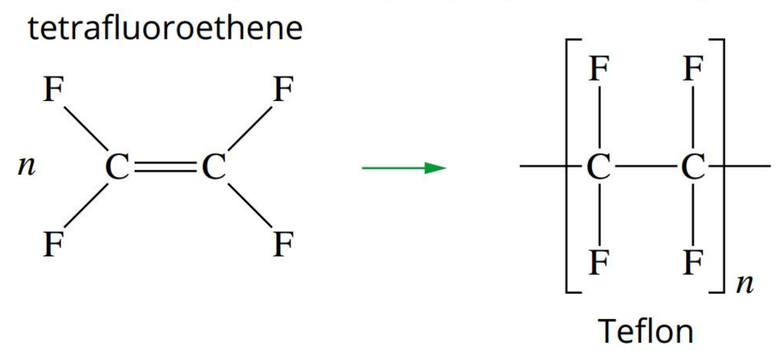


FIGURE 10.4.13 Addition polymerisation of tetrafluoroethene makes the polymer Teflon.

Molecules of tetrafluoroethene react with themselves to form the polymer polytetrafluoroethene, known as Teflon™. Teflon has quite exceptional properties that are very different from those of polyethene. Teflon can be used to make non-stick frying pans, medical implants and gears. The electronegative fluorine atoms reduce the strength of intermolecular bonds with other substances.

Another innovative application of Teflon is in Gore-Tex® (Figure 10.4.14). Gore-Tex is a fabric that 'breathes'. Rain cannot penetrate a Gore-Tex raincoat, but water vapour from sweat can escape through it. High-quality camping clothing is often made from Gore-Tex.

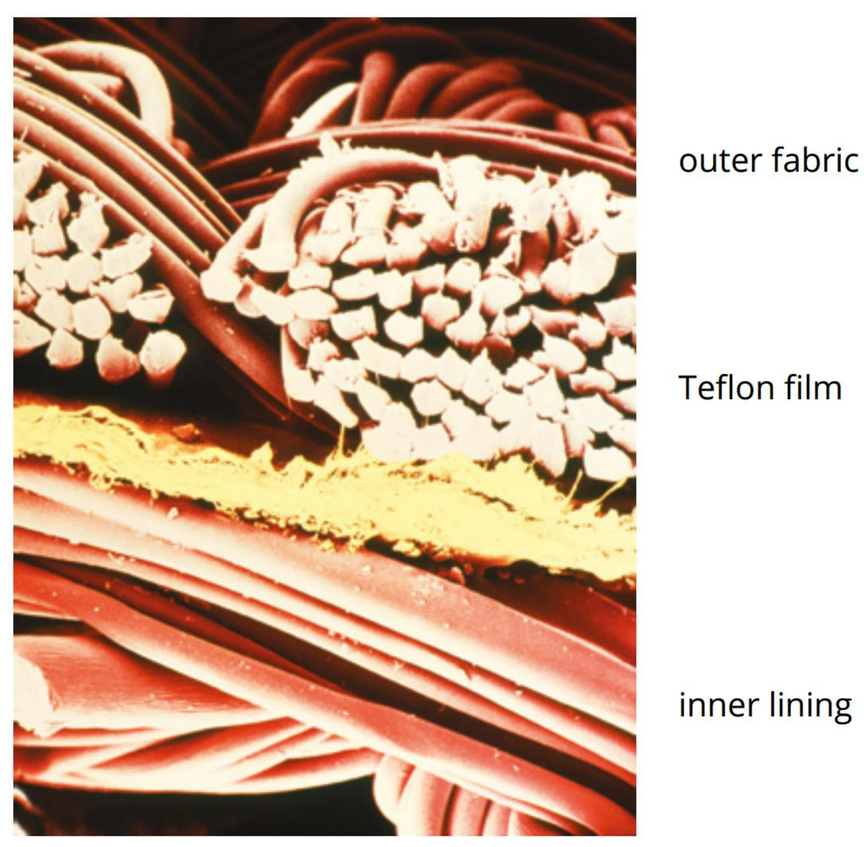


FIGURE 10.4.14 Scanning electron micrograph of Gore-Tex fabric. The small yellow and white particles are Teflon. The small holes between these particles allow vapour to pass through the fabric, but not liquid.

The properties of Teflon are summarised in Table 10.4.2.

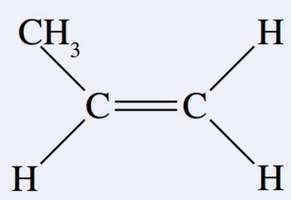
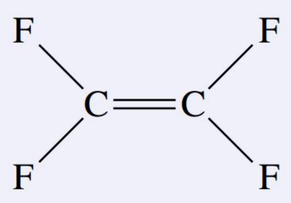
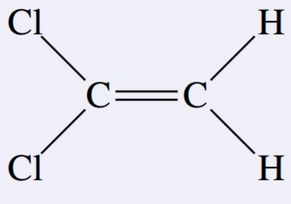
TABLE 10.4.2 A summary of the properties of Teflon

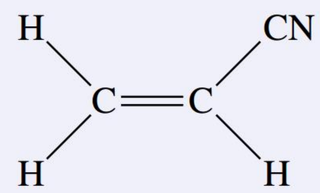
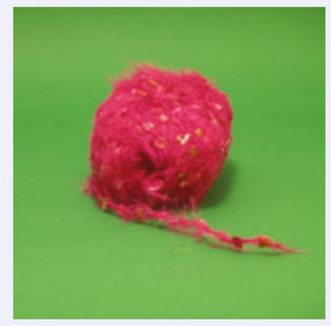
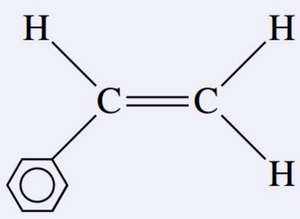
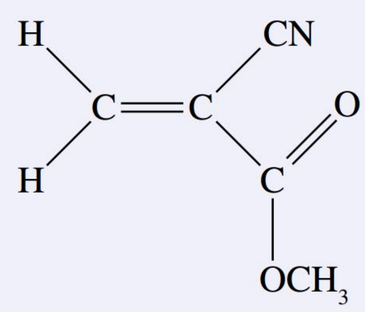
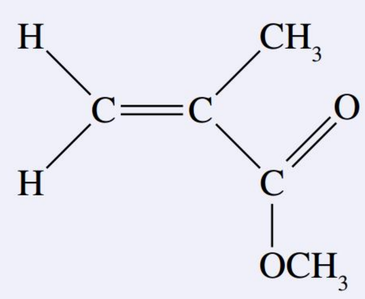
Property	Description
non-stick	Teflon repels all other substances, both hydrophobic (oil, fat) and hydrophilic (water).
heat-resistant	The melting point of Teflon is 335°C and the upper operating temperature for this polymer is 260°C.
chemical-resistant	Teflon is extremely resistant to all known chemicals. It is not attacked by strong acids and bases and is inert towards all organic solvents.
good mechanical properties	Teflon is strong and durable, but not as hard as PVC.
low friction coefficient	Teflon is slippery to the touch. The friction coefficient between two pieces of Teflon is very low.
flame-resistant	Teflon is non-flammable.

Other addition polymers

In the Senior Chemistry syllabus, you are required to understand the structural features of three key addition polymers (polyethene, polypropene and polytetrafluoroethene); however, there are thousands of commercial addition polymers. Table 10.4.3 shows a number of other polymers that may be familiar to you. The mix of functional groups and elements used leads to each polymer offering a unique set of properties that make them of commercial interest.

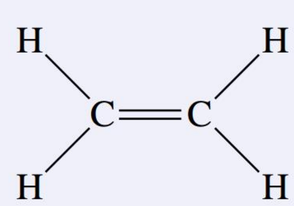
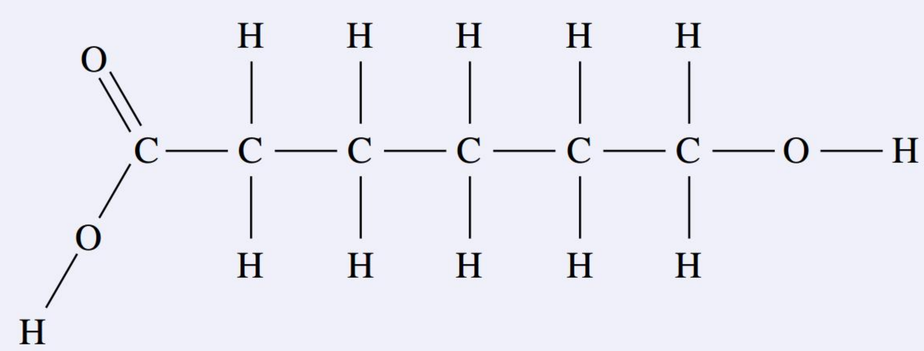
TABLE 10.4.3 Commercial addition polymers

Monomer	Polymer	Properties	Examples
propene	polypropene (polypropylene)	durable, cheap	artificial grass, dishwasher-safe plastic, ice-cream containers, rope
			
tetrafluoroethene	polytetrafluoroethene (PTFE, Teflon™)	non-stick, high melting point	frying pan and iron coatings, plumber's tape, Gore-Tex® fabric
			
dichloroethene	polyvinylidene chloride (PVDC)	sticks to self, transparent, stretchy	food wrap
			

Monomer	Polymer	Properties	Examples
propenenitrile	polypropenenitrile (acrylic)	strong, able to form fibres	acrylic fibres, fabrics
			
phenylethene (styrene)	polyphenylethene (polystyrene)	hard, brittle, low melting point	toys, packaging, expanded foams
			
methylcyanoacrylate	polymethylcyanoacrylate	polymerises on contact with water	superglue
			
methyl 2-methylpropenoate	polymethyl methacrylate	transparent, strong	Perspex™ (a glass substitute)
			

In this section, you have seen there are two different mechanisms for the formation of polymers, condensation polymerisation and addition polymerisation. The key features of each process are summarised in Table 10.4.4.

TABLE 10.4.4 Comparison of the monomers used for addition and condensation polymerisation

Addition polymerisation	Condensation polymerisation
 Monomer has a carbon–carbon double bond. Double bond breaks during polymerisation. Polymer chain contains single C–C only. No other product formed.	 Functional group on each end of the monomer. Functional groups react. Polymer chain will contain atoms other than C. Smaller molecules, such as water, formed.

10.4 Review

SUMMARY

- A polymer is a covalent molecular substance composed of many small molecules joined together.
- A monomer is the smallest molecule that reacts with another monomer, of either the same compound or a different compound, to form the polymer.
- To simplify the drawing of the polymer, the repeating unit within the polymer is enclosed within large square brackets with a subscript used to indicate the number of repeated units.
- There are two main types of polymers—addition polymers and condensation polymers.

Addition polymerisation	Condensation polymerisation
monomers contain double or triple covalent bonds	monomers have at least two functional groups
no by-products	small molecules such as water and HCl produced
polymer chain contains only carbon atoms	polymer chain includes atoms other than carbon

- Condensation polymers, such as nylon, are formed when molecules with two functional groups meet and react together, eliminating a small molecule (often water). The term nylon refers to condensation polymers where the monomers are linked by amide bonds (also known as polyamides), while polyester monomers are linked by ester bonds. Carbohydrates and proteins are natural condensation polymers.
- Addition polymers are formed when the carbon-to-carbon double or triple bonds in the monomers break, providing electrons for the monomers to join. Polyethene, polypropene and polyvinyl chloride are examples of widely used addition polymers.
- There are three possible arrangements of the side groups of polypropene, referred to as isotactic, atactic and syntactic. The regular arrangement of the side groups in polypropene increases the strength of the polymer due to greater intermolecular forces.
- A copolymer is formed from a reaction between two different monomers.

KEY QUESTIONS

Describe

1 Define polymerisation.

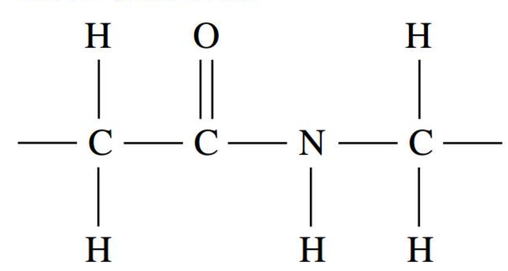
2 **a** Why is butane unsuitable as an addition polymerisation monomer?

b Why is butanoic acid unsuitable as a condensation polymerisation monomer?

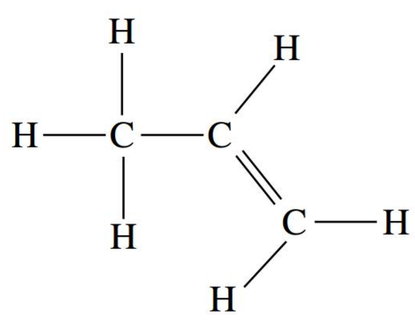
Apply

3 Draw the structure of a syntactic polypropene chain.

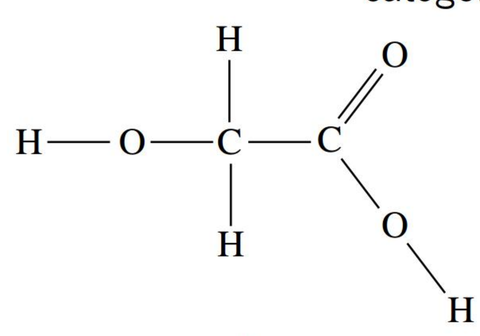
4 The polymer segment shows the link formed between two monomers. Draw two functional groups that could form this link.



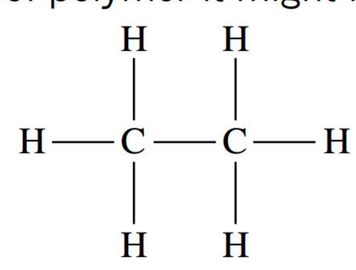
5 Examine each of the four molecules shown below and identify if the molecule could be a monomer. If the molecule is suitable for polymerisation, state which category of polymer it might form.



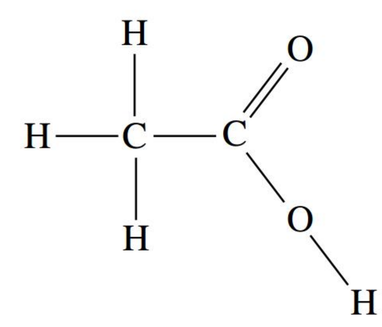
a



b



c



d

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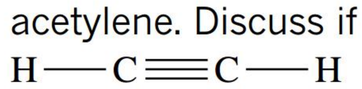
10.4 Review *continued*

6 The molecule shown is ethyne, commonly called acetylene. Discuss if ethyne is suitable as a monomer.



7 Describe the essential differences between the monomers that form addition polymers and the monomers that form condensation polymers. Include in your answer an example of each.

8 Draw the reaction scheme and general structure of the polymer formed in the reaction between alcohols and carboxylic acids.

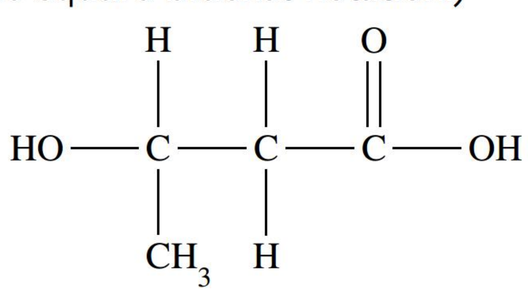
Analyse

9 A 100 kg sample of ethene is reacted to form polyethene. A 100 kg sample of nylon monomer is also reacted to form a polymer.

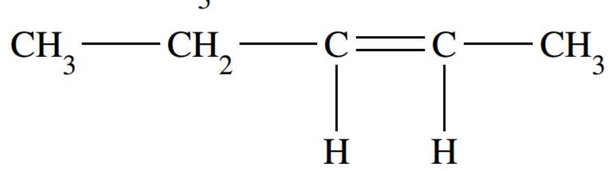
Assuming complete polymerisation of both samples, compare the mass of the product formed from each reaction.

10 For each of the following monomers, provide the structural formula of the polymer that is formed. (Hint: use square bracket notation.)

a



b



11 From the structures of the repeating units of the polymers below, provide a condensed structural formula for the monomers from which they were produced.

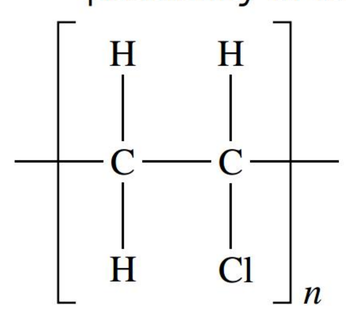
(Hint: draw a structural diagram of each segment first.)

a $-[CH_2-CH_2]-$

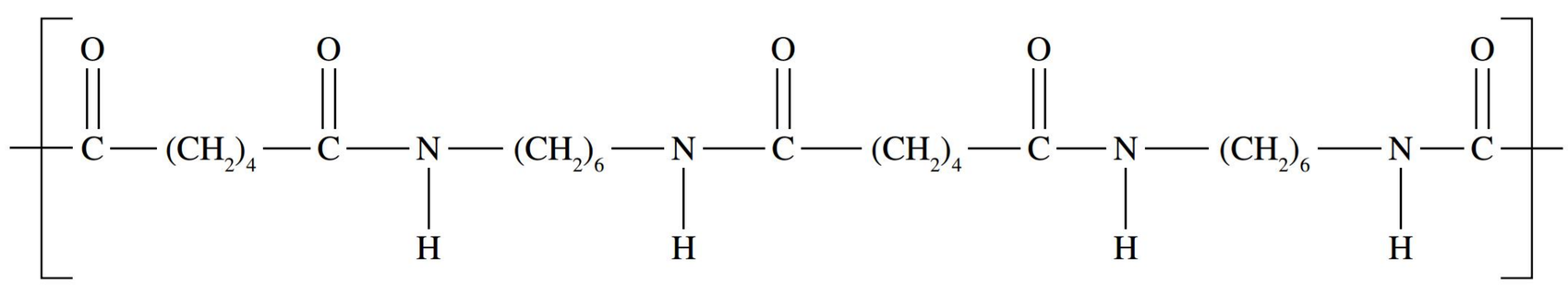
b $-[CO-CH(CH_3)NH]-$

c $-[NH(CH_2)_6NH-CO-(CH_2)_4CO]-$

12 The terms isotactic, atactic and syntactic are related to the relative geometric arrangement of the side groups. Deduce if polyvinyl chloride, shown below, has the possibility of forming similar variations of structure.

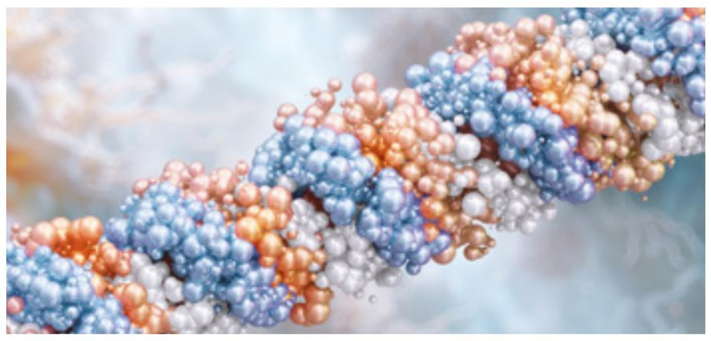


13 Like the amino acid monomers that link to form a polypeptide, the monomers used to make nylon-6,6 have two functional groups. Examine the nylon-6,6 structure in the diagram below to identify and draw structures for the two monomers that are used to synthesise nylon-6,6.



10.5 Effect of structure on properties of synthetic and natural polymers

We have seen in the previous sections that polymers are diverse materials. Their long molecules can be formed by either addition or condensation reactions. Condensation polymers can be formed synthetically or in living things. Figure 10.5.1 is a representation of polymer types, listing examples of each category. Hopefully, you can start at the top of the flow chart and visualise the structural features of each branch shown. Table 10.5.1 shows a segment of a sample polymer from the three main categories of polymers that this chapter focuses on.



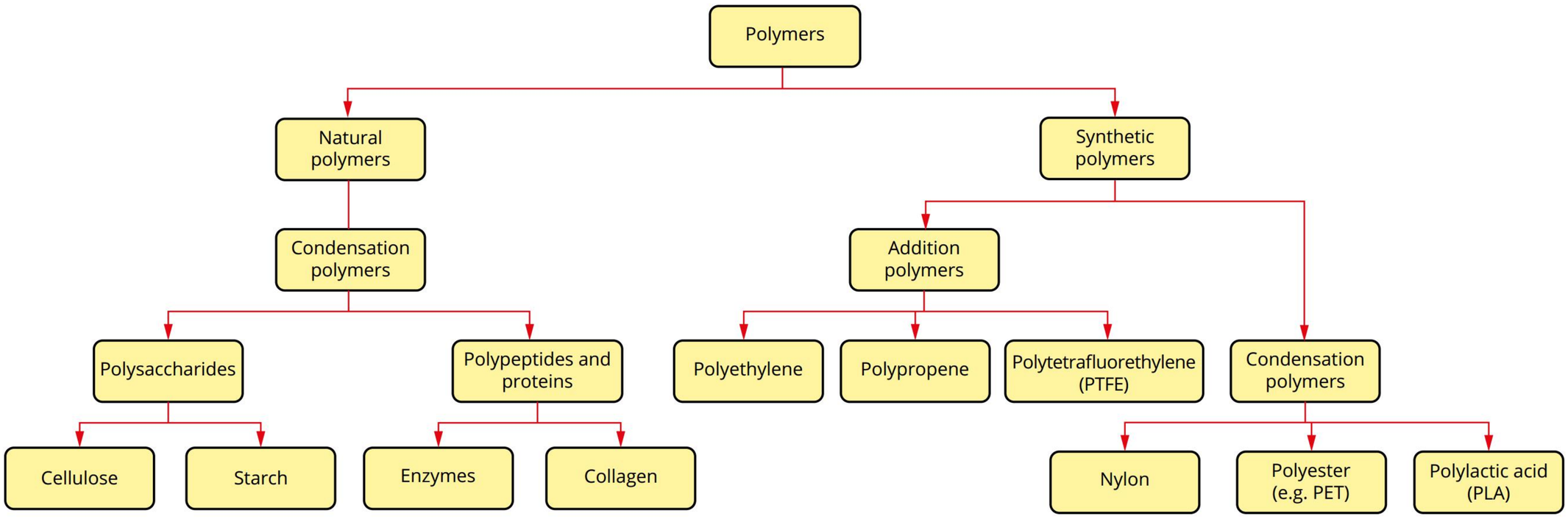
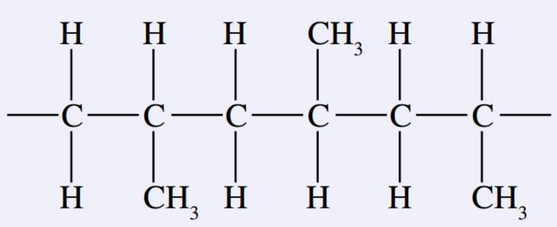
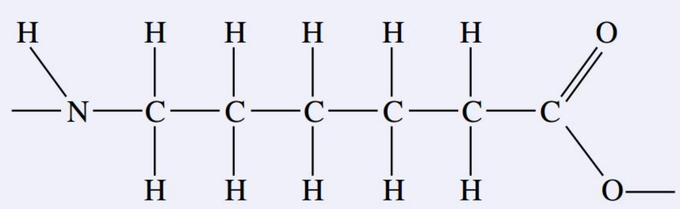
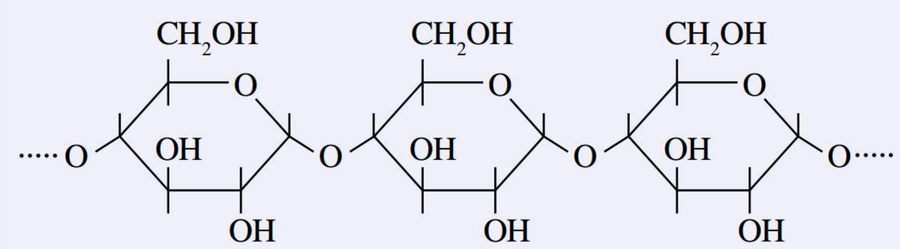


FIGURE 10.5.1 Flow chart showing a classification of polymers

TABLE 10.5.1 Key polymer categories showing an example molecule for each category and the feature of the monomer that enables polymerisation

addition polymer	condensation polymers	
		
polypropene (syntactic)	synthetic polymer: nylon	natural polymer: starch
C=C bond in monomer	functional group on each end of monomer ($-NH_2$ and –COOH)	functional group on each end of monomer (HO– and –OH)

The structures of natural polymers are often more complex than synthetic ones. Figure 10.5.2, for example, shows the structure of chitin, a polymer that is found in the cell walls of fungi and is the main component of the exoskeleton of crustaceans and insects. Research scientists are regularly finding new medical-related uses for chitin, including drug capsule casing and wound dressing material.

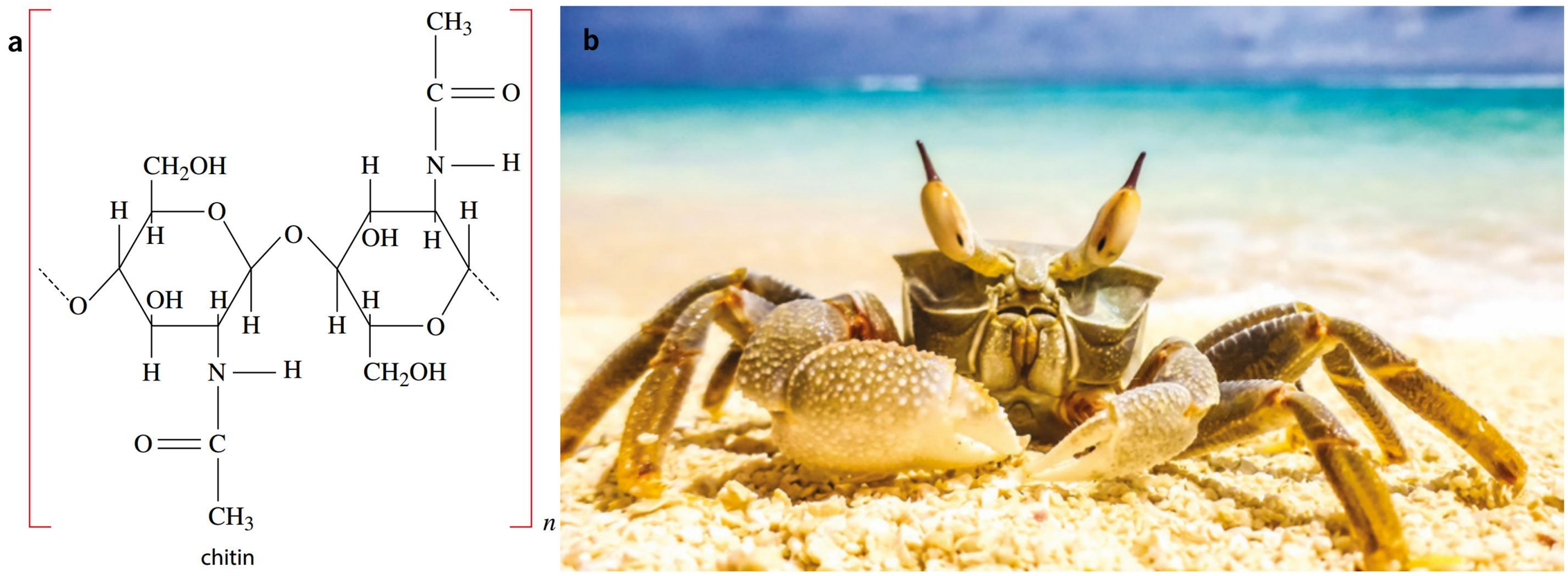


FIGURE 10.5.2 (a) The chemical structure of chitin. The condensation polymerisation reaction occurs within the organism. (b) Chitin is the main component of the exoskeletons of crustaceans and insects.

POLYMER PROPERTIES

When it comes to polymer properties, it is definitely not a case of 'one size fits all'. Intensive research by chemists has enabled them to tailor the properties of a particular polymer to meet the exact requirements of its end use. To do this, chemists vary:

- whether or not there are covalent bonds (cross-links) between polymer molecules
- the length of polymer chains
- the degree of branching along chains
- the choice of monomer
- other additives used in the product, such as foaming agents, plasticisers and antioxidants.

The strategies above allow scientists to engineer important properties of the product, such as melting point, strength and density. There is also an increased urgency to improve the sustainability of the plastics industry to limit the use of dwindling petroleum reserves as monomers and to lessen the pollution caused by waste plastics and microplastics. Chemists aim to do this by developing functional polymers that are recyclable and biodegradable.

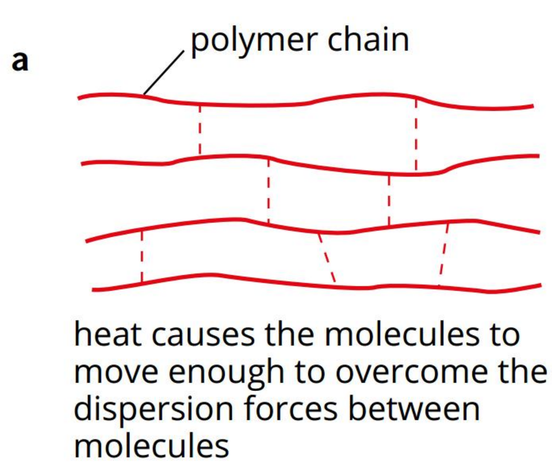


FIGURE 10.5.3 (a) A thermoplastic polymer has weak bonds between the chains. (b) Thermoplastic polymers are often used to make plastic bottles and food packaging.

Thermoplastic and thermosetting polymers

Polymers can be classified into two groups based on their behaviour when heated:

- **thermoplastic** polymers
- **thermosetting** (or thermoset) polymers.

Thermoplastic polymers soften when heated, which means they can be remoulded or recycled. Polymers are thermoplastic if the bonds between the long polymer chains are hydrogen bonds, dipole–dipole bonds or weak dispersion forces (Figure 10.5.3). When heated, the molecules in thermoplastic materials gain enough energy to overcome the intermolecular forces and become free to move and slip past one another. If the polymer can be remoulded, then it can probably be recycled, which is an important property in modern society.

Some condensation polymerisation reactions produce a three-dimensional structure, rather than a linear molecule. Lignin, shown in Figure 10.5.4, is an example. It is a natural polymer produced alongside cellulose in plants, where both polymers combine to provide the structural material in plants. Covalent bonds between polymer molecules are called cross-links.

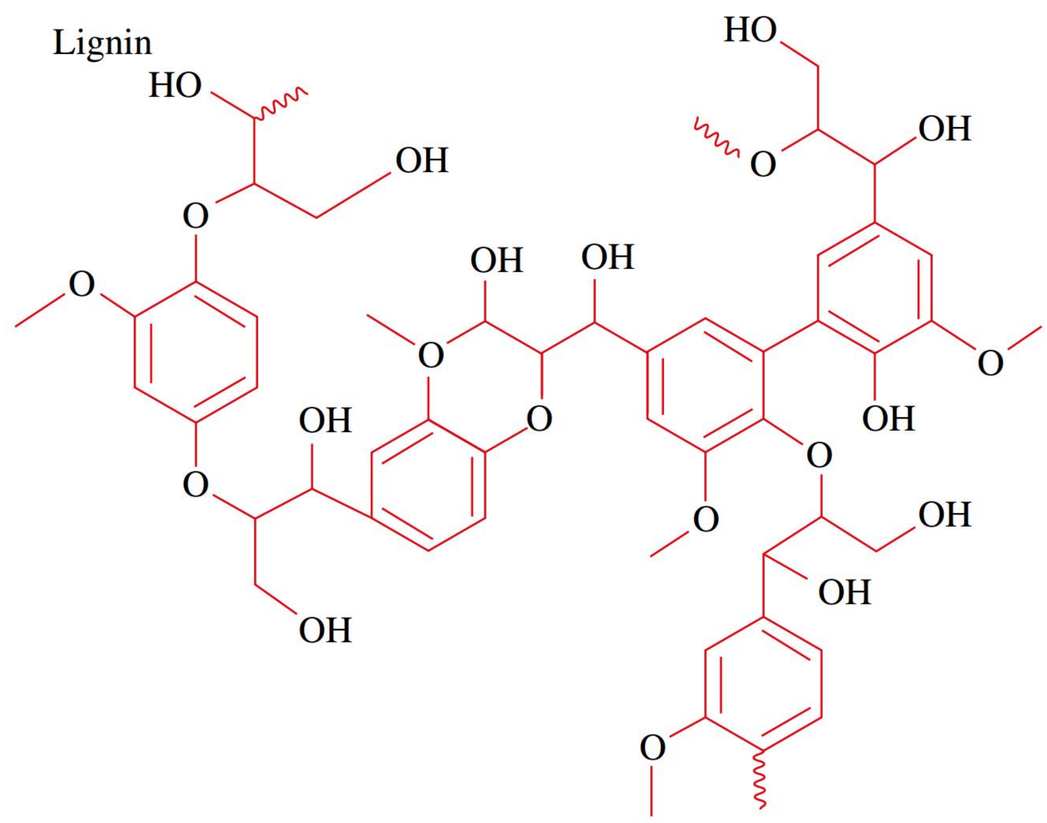


FIGURE 10.5.4 Lignin is a cross-linked polymer. Monomers form a three-dimensional structure rather than long molecules.

Cross-links limit movement between the polymer molecules and make the polymer rigid, hard and heat-resistant. Thermosetting polymers are used to make items such as saucepan handles, bowling balls and shatterproof crockery (Figure 10.5.5b). Thermosetting polymers decompose or char when heated. They do not soften or melt as their structure does not have long molecules held together by intermolecular forces. If the temperature becomes high enough to break the covalent bonds, the breaks may be at any point, causing the polymer to decompose (Figure 10.5.5a). It is difficult to recycle thermosetting polymers as they cannot be remoulded into new products.

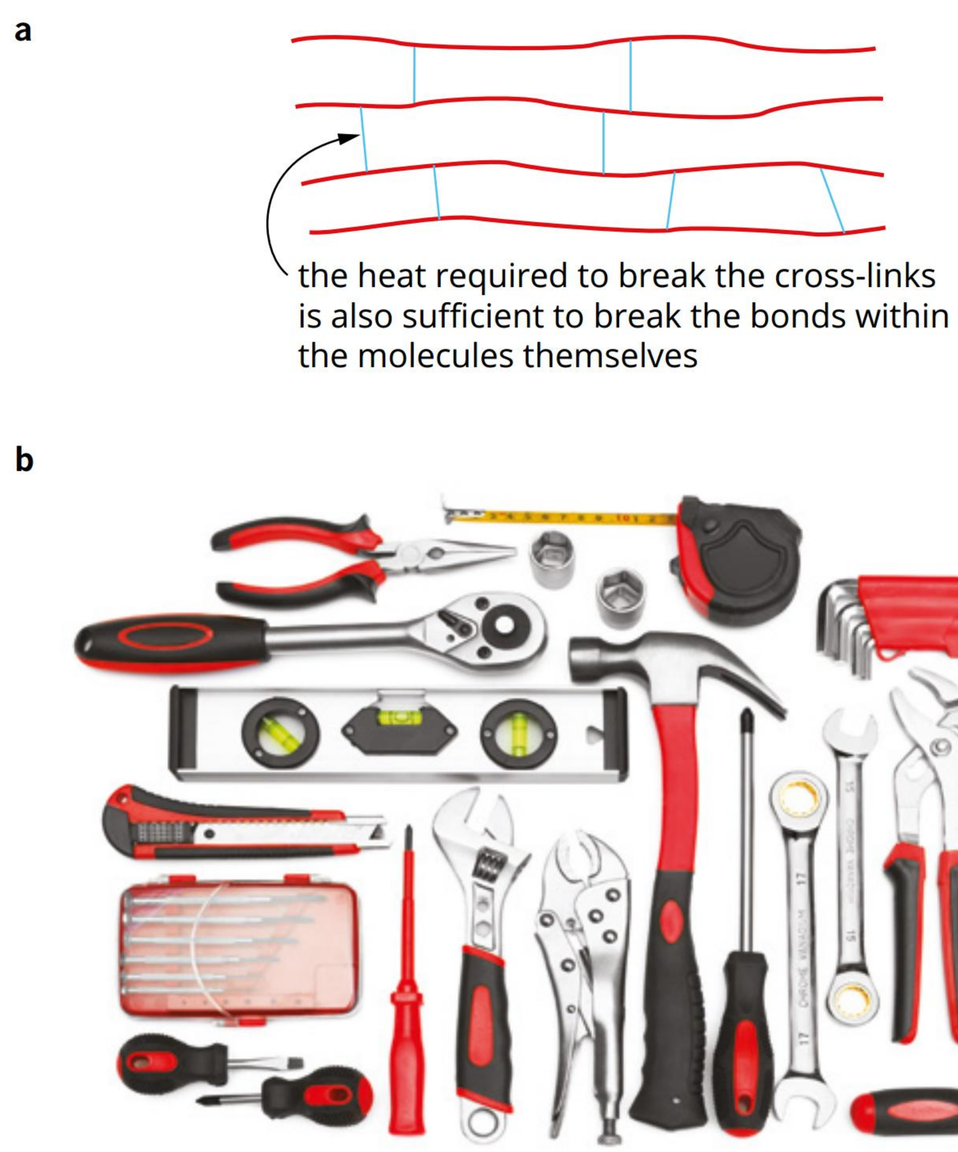


FIGURE 10.5.5 (a) A thermosetting polymer has strong covalent bonds between the chains. (b) A variety of products are made from thermosetting polymers.

Chain length

Polymers are made of strands of individual polymer chains that interact and pass over each other. Thus, the physical properties of polymers are strongly dependent on the length of the polymer chain.

As the length of polymer chains increases,

- the tangling between the molecules increases
- the number of intermolecular forces increases
- the melting point increases
- the strength and toughness increases.

As a rule, mechanical properties such as ductility, tensile strength and hardness rise and eventually reach a maximum with increasing chain length.

The effect on properties of increased chain length can be seen by comparing ultra-high molecular weight polyethene (UHMWPE) with common forms of polyethene such as low-density polyethene, LDPE. The careful use of catalysts allows much longer molecules to form in UHMWPE. The impact on melting points and toughness of the longer molecules can be seen in Table 10.5.2.

TABLE 10.5.2 Impact of chain length on polyethene properties

	LDPE	UHMWPE
number of ethene monomers in a molecule	700–1800	> 100 000
melting point, °C	105–108	130–136
uses	plastic bags, containers	bulletproof vests, safety helmets

Branching

LDPE

The earliest method of producing polyethene involved high temperatures (around 300°C) and extremely high pressures. Under these harsh conditions, the polymer is formed too rapidly for the molecules to be neat and symmetrical. Figure 10.5.6 shows that the product contains many small chains, called branches, that divide off from the main polymer.

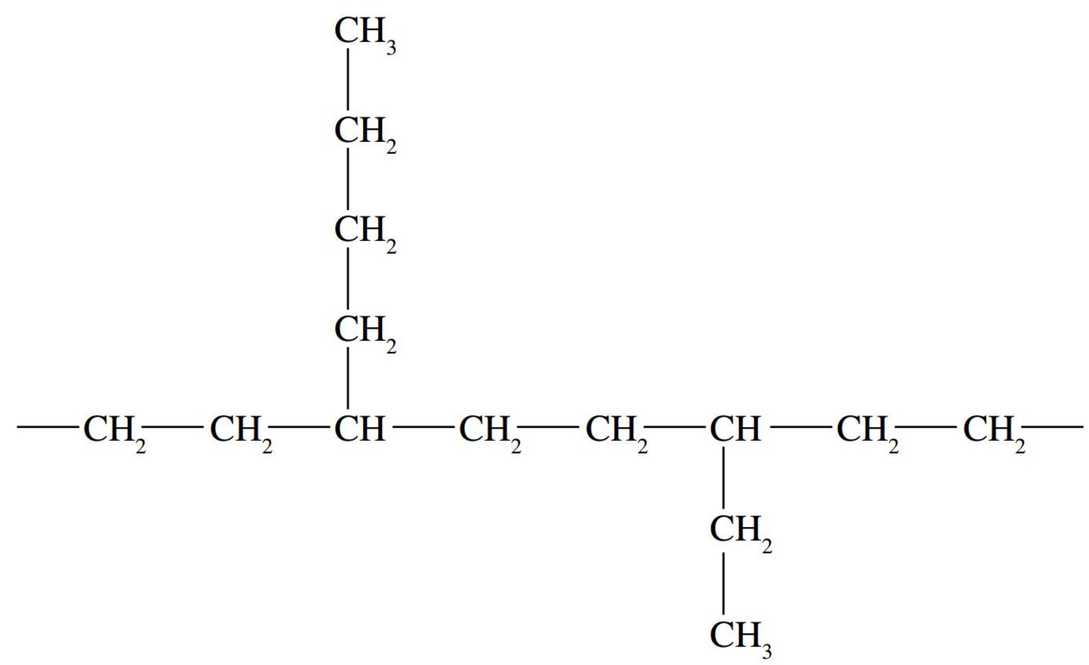


FIGURE 10.5.6 Polyethene made under high pressure and at high temperatures has short branches off the main chain.

The presence of these branches impacts the properties of the polymer as the molecules cannot pack closely together. The dispersion forces between molecules are weaker when the molecules are further apart. The arrangement of the polymer molecules can be described as disordered or non-crystalline. This form of polyethene is known as **low-density polyethene** or LDPE. Its structure and an example of its use are shown in Figure 10.5.7. The properties of LDPE include that it:

- has low density
- is relatively soft
- has a low melting point
- is non-crystalline
- is opaque
- is a non-conductor of electricity.

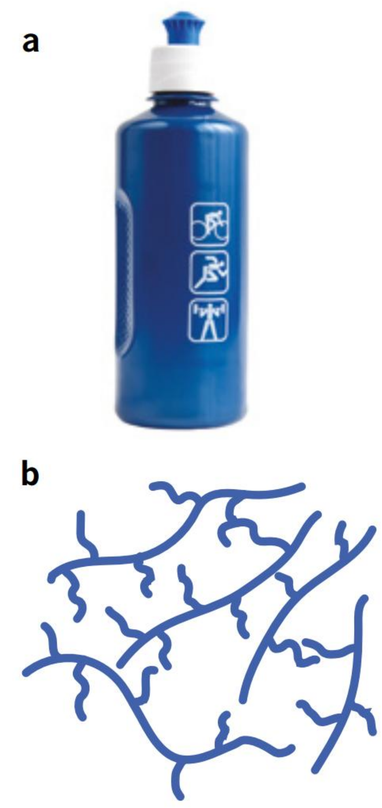


FIGURE 10.5.7 Low-density polyethene: (a) a drink bottle made from LDPE and (b) LDPE branched structure

HDPE

A low-pressure method of producing polyethene was developed by the Union Carbide company in the late 1960s. Highly specialised transition metal catalysts, known as **Ziegler–Natta catalysts**, are used to avoid the need for high pressures. The polymer molecules are produced under much milder conditions and there are very few branches.

The lack of branches allows the molecules to pack together tightly, increasing the density and the hardness of the polymer formed. The arrangement of the polymer molecules is more ordered, resulting in crystalline sections. This form of polyethene is known as **high-density polyethene** or HDPE. Its structure and its uses are shown in Figure 10.5.8. The properties of HDPE include that it:

- has high density
- is hard
- has a relatively high melting point
- has crystalline sections.

Table 10.5.3 compares the structure and properties of the two common forms of polyethene. The difference in density between the two forms is typically 0.91–0.94 g cm^{-3} for LDPE compared to 0.93–0.97 g cm^{-3} for HDPE.

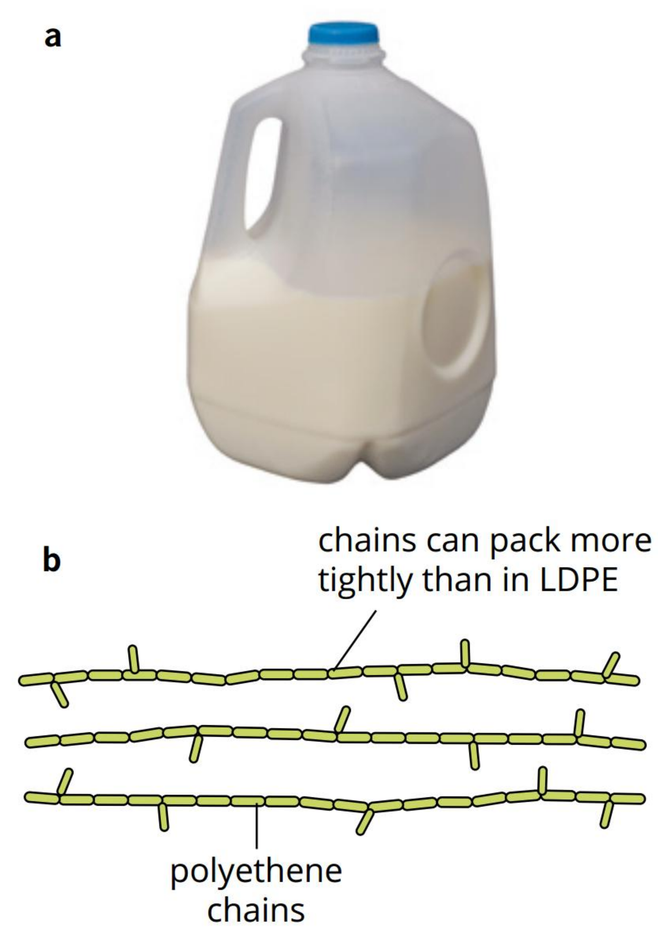


FIGURE 10.5.8 High-density polyethylene: (a) a bottle made from HDPE and (b) HDPE structure

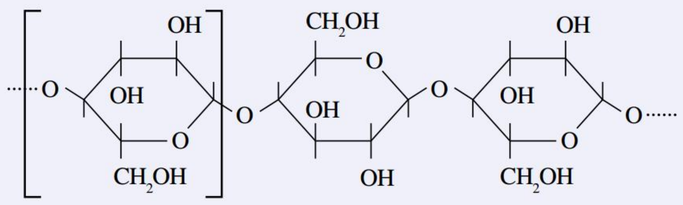
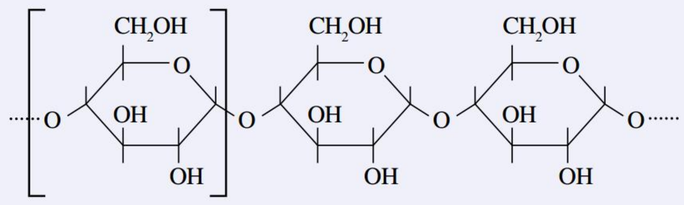
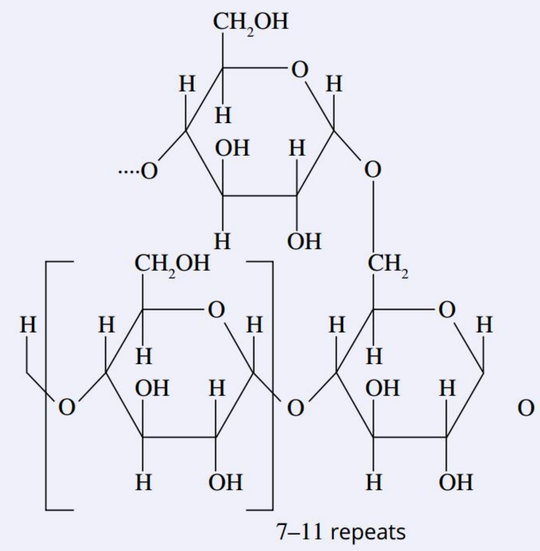
TABLE 10.5.3 A comparison of highly crystalline HDPE with an amorphous LDPE

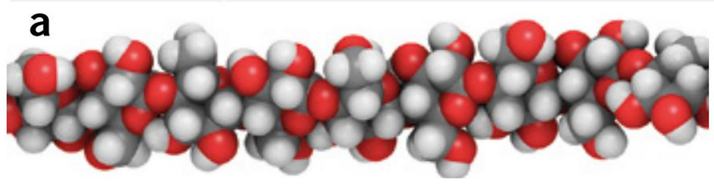
HDPE	LDPE
• catalysts used to control the polymerisation reaction • long molecules, few branches • molecules pack tightly • stronger dispersion forces • higher tensile strength • can be rigid or flexible • opaque	• formed at high temperature and pressure • polymerisation not controlled • molecules contain many branches • molecules cannot pack tightly • weaker dispersion forces • lower tensile strength • flexible • transparent

Branching in natural polymers

The impact of branching on polymer properties is evident with natural polymers such as polysaccharides and polypeptides. Cellulose, starch and glycogen are all polymers of glucose but their structural differences lead to their different roles in living things (Table 10.5.4).

TABLE 10.5.4 Key carbohydrate structures showing properties and uses

	structure	properties	use
cellulose	 alternating $-CH_2OH$ groups		 frequent cross-links
starch (amylose)	rigid, strong, insoluble in water	powdery white solid	powdery white solid
glycogen	structural material in plants	energy storage molecule in plants	energy storage molecule in animals



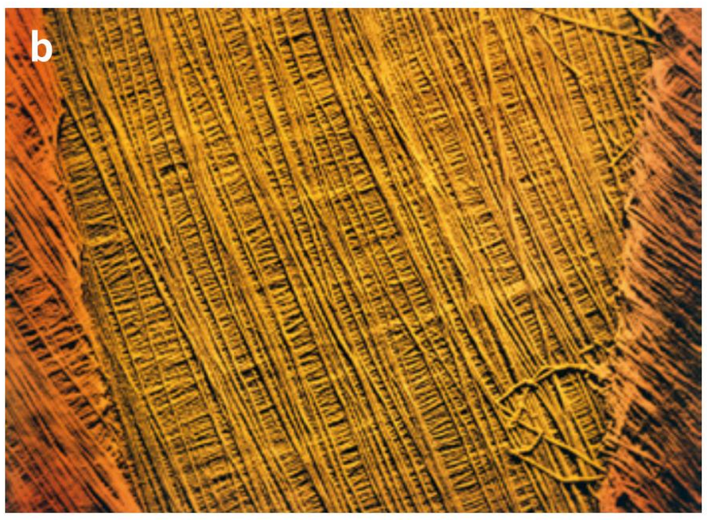
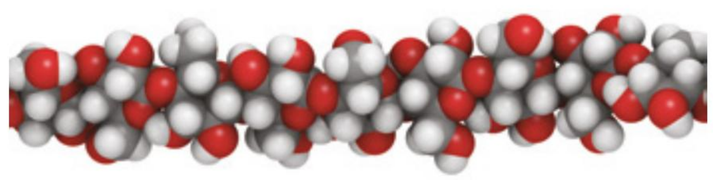


FIGURE 10.5.9 (a) This model shows the linear nature of a cellulose molecule. The oxygen atoms in the hydroxyl groups are coloured red. (b) A scanning electron microscope image shows the cellulose fibres in the walls of algae cells.

The alternating nature of the $-CH_2OH$ groups in cellulose allows for neat alignment of hydroxyl groups between neighbouring cellulose molecules. The result is hydrogen bonding between the molecules, producing a strong material that gives the plant support and rigidity. The linear nature of cellulose fibres is shown in Figure 10.5.9. Despite also being formed from glucose monomers, neither glycogen nor starch is considered a strong material as their molecules do not pack tightly.

The effect of polymer molecule alignment is also evident in a comparison between collagen and enzymes (Figure 10.5.10). Both are proteins formed from amino acids but the arrangement of the molecules is very different, allowing both to perform different functions in living things.



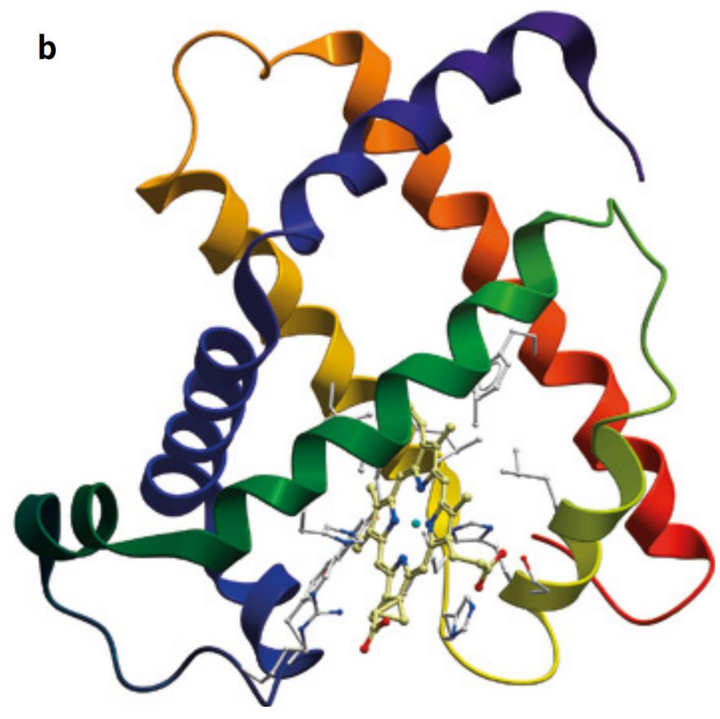


FIGURE 10.5.10 (a) The protein molecules in collagen are linear, allowing them to pack tightly together. (b) The protein molecules in an enzyme are not packed as tightly.

Collagen is the most abundant protein in the body. It provides strength and structure to various tissues, such as cartilage, skin and bones. There are several types of collagen, but in general, they feature three parallel polypeptide strands wound into a helical structure. The tight packing of the strands gives it a toughness that an enzyme does not have or need. The collagen and cellulose examples show that if the function of a natural polymer requires strength or toughness, nature will align the molecules in tightly fitting linear structures.

Choosing a monomer to change polymer properties

Polyethene is the most used polymer in the world, due to its relatively low cost and versatility. Many applications, however, require polymers with more specialised properties than polyethene. One way to improve the properties of polyethene is to replace one or more hydrogen atoms on the ethene monomer with more electronegative atoms, or with a larger group of atoms.

Ethene is non-polar, meaning that the intermolecular forces present between polyethene molecules are weak dispersion forces. Polyvinyl chloride (PVC) is made from the polymerisation of chloroethene ($CHCl{=}CH_2$), as shown in Figure 10.5.11.

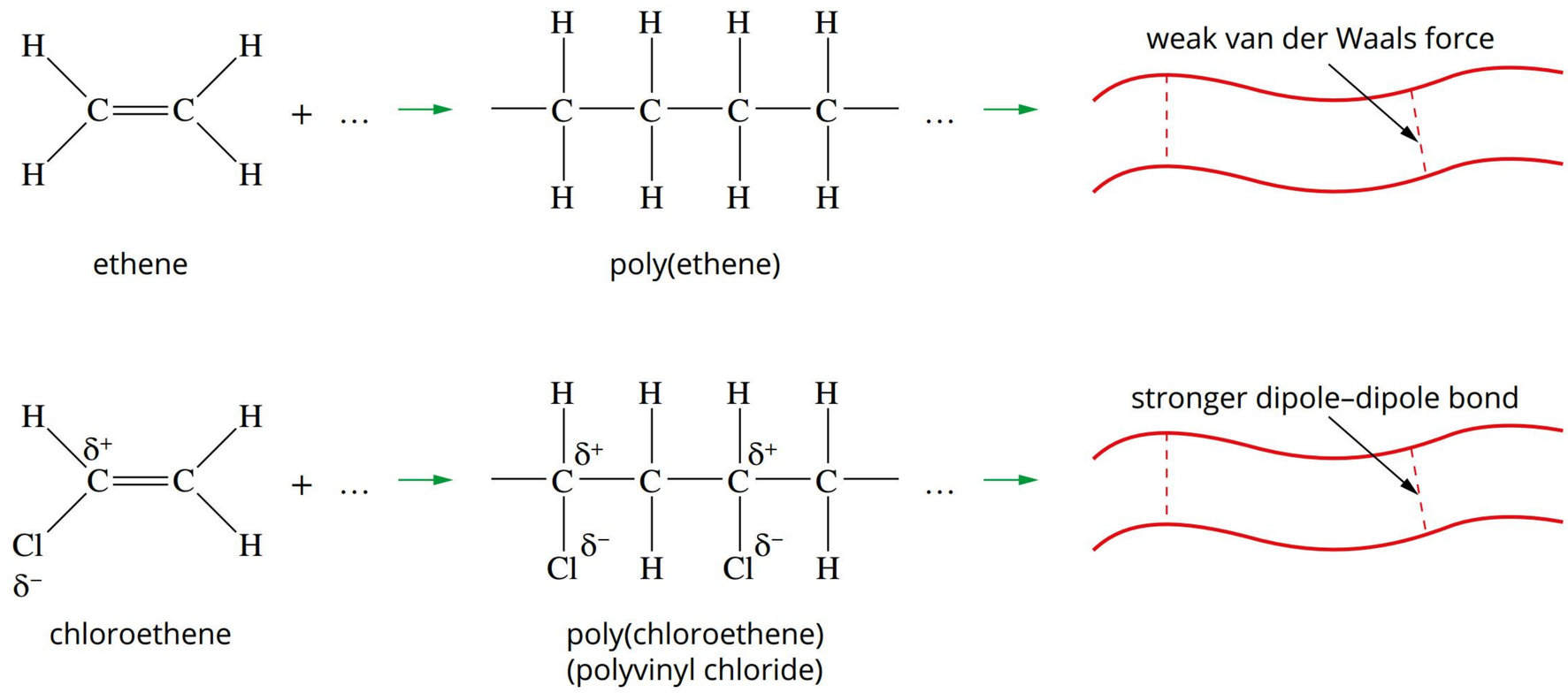


FIGURE 10.5.11 Polyvinyl chloride (PVC) is formed from polymerisation of polar chloroethene monomers, and has dipole–dipole attractions between chains.

The carbon–chlorine bonds in a PVC molecule are polar and allow dipole–dipole attractions to occur between polymer chains. Because of this, PVC is harder and more rigid than polyethene. It has a low electrical conductivity and a low flammability. A PVC item burning in a flame will stop burning when it is removed from the flame. PVC is used in conveyor belts, cordial bottles, water pipes and the covering of electrical wiring.

As the polarity of the side groups in a monomer increases, the melting point and toughness are likely to increase. This trend is evident when hydrogen bonds occur between polymer molecules. Hydrogen bonds are the strongest intermolecular forces and, as you learnt in Unit 2, these require a hydrogen atom on one polymer, molecule or chain interacting with a highly electronegative atom, nitrogen, oxygen or fluorine, on another polymer, molecule or chain. For instance, in nylon, there are NH groups that can form hydrogen bonds with the C=O groups of another chain. The large number of interchain hydrogen bonds makes the nylon polymer relatively stiff. These forms of bonding are summarised in Table 10.5.5.

TABLE 10.5.5 Summary of the three types of intermolecular forces

	Dispersion forces	Dipole–dipole forces	Hydrogen bonding
definition	• attraction between two instantaneous dipoles • asymmetrical electron distribution • all atoms and molecules	• attraction between two permanent dipoles • polar molecules	• attraction between molecules with N–H, O–H and F–H bonds • extremely polar bonds—very strong dipole–dipole forces
diagram	δ– δ+ H - - - - - - H δ– δ+ H - - - - - - H	δ+ δ– H Cl δ+ δ– H Cl	δ– δ+ O H H δ– δ+ O H H
relative strength	• weakest	• medium strength	• strongest
polymers with this bonding as the strongest bond type	• polyethene • polypropene	• polyvinyl chloride • polyester	• nylon • protein • cellulose
other information	• increase in strength as molar mass increases (more electrons)	• stronger when molecules are closer together	• no chemical bonding

Size of side group on monomer

The side group in styrene is a flat ring of six carbon atoms, often called a benzene ring, as shown in Figure 10.5.12.

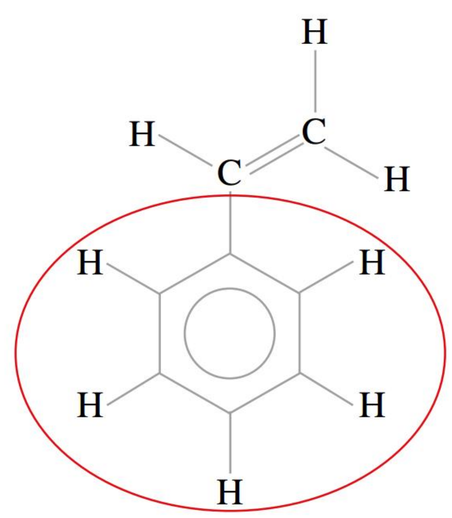


FIGURE 10.5.12 The chemical structure of the styrene monomer showing the bulky side group circled in red

Styrene polymerises as shown in Figure 10.5.13, where benzene rings are covalently bonded to every second carbon atom in the polymer chain. The bulky side groups in the polymer chains make it difficult for the chains to slide over one another or stack closely together. This causes polystyrene to be a hard but quite brittle plastic with a low density. It is used to make food containers, picnicware and refrigerator parts.

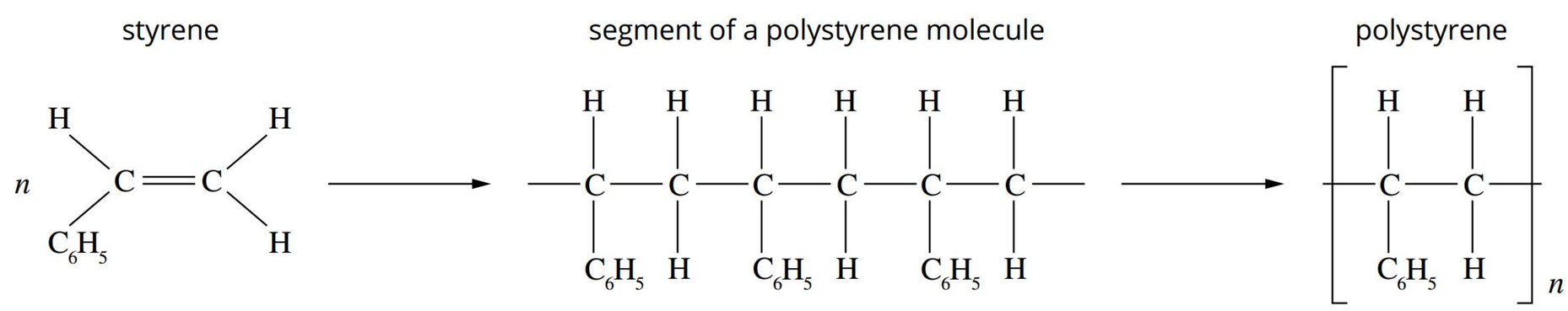


FIGURE 10.5.13 The polymerisation of styrene to form polystyrene

Biodegradability

There is a price to pay for the durability of plastic items – they can persist in landfill for a long time.

Australians consume more than 1.5 million tonnes (1.5 billion kilograms) of polymer materials every year, which includes many different plastics. The disposal of waste polymer materials is a serious issue in our society. Images such as those shown in Figure 10.5.14 are an all-to-familiar sight around the world. In Australia, the percentage of plastic products recycled is still less than 20%.

Awareness is also increasing that plastics in water systems are breaking down into smaller particles, classified as microplastics. Microplastics have particles up to 5 mm in diameter, they can last for thousands of years and they are toxic to marine life. Their presence in marine life is leading to the detection of increased levels of microplastics in humans.

FIGURE 10.5.14 (a) Plastic persists for a very long time in the environment. (b) Waste plastic waiting to be recycled.

Waste terminology

The following terms will be helpful to your understanding of plastics sustainability:

- **Biodegradable**: Biodegradation is a chemical process during which microorganisms that are available in the environment convert materials into natural substances such as water, carbon dioxide and compost. The problem with the term biodegradable is the lack of a time frame. In an oxygen-scarce landfill site, many plastics labelled as biodegradable simply do not degrade. In addition, on-site biodegradation requires the presence of capable microorganisms.
- **Compostable**: A product that is capable of disintegrating into natural elements in a compost environment, leaving no toxicity in the soil. The term compostable is being used to identify materials that really do degrade (in approximately 90 days) under normal conditions. Common soil microorganisms are able to digest the polymer.
- **Recyclable plastics**: Products that can be remoulded and used again.

> **i** Biodegradable materials are converted to smaller molecules and then to water and carbon dioxide in the presence of common soil microorganisms over a time frame dependent on many factors. Compostable products will biodegrade naturally within 90 days and leave no harmful substances in the soil.

Condensation polymers such as PET and natural polymers are more likely to be biodegradable than addition polymers due to the presence of oxygen in the molecule chain. The polarity of the C=O bond makes it susceptible to attack from enzymes and microorganisms. The ester or amide group is hydrolysed in the presence of water. While all condensation polymers are likely to be degraded by hydrolysis in this way, the extent of biodegradation of a polymer will also depend on the three-dimensional structure of the macromolecules (that makes the ester or amide group accessible to water) and also on the microorganisms and enzymes present (see example below).

PET would normally take over 400 years to degrade naturally, but Japanese scientists discovered bacteria in 2016 in a particular landfill site that were breaking down plastic products at six times the normal rate. They have isolated an enzyme produced by the bacteria that they named PETase. Figure 10.5.15 shows the enzyme attacks the covalent bonds linking the monomers (the ester bonds) in PET polymer items. This process leads to the monomers reforming, offering the possibility of reusing the monomer to build the plastic into a new product.

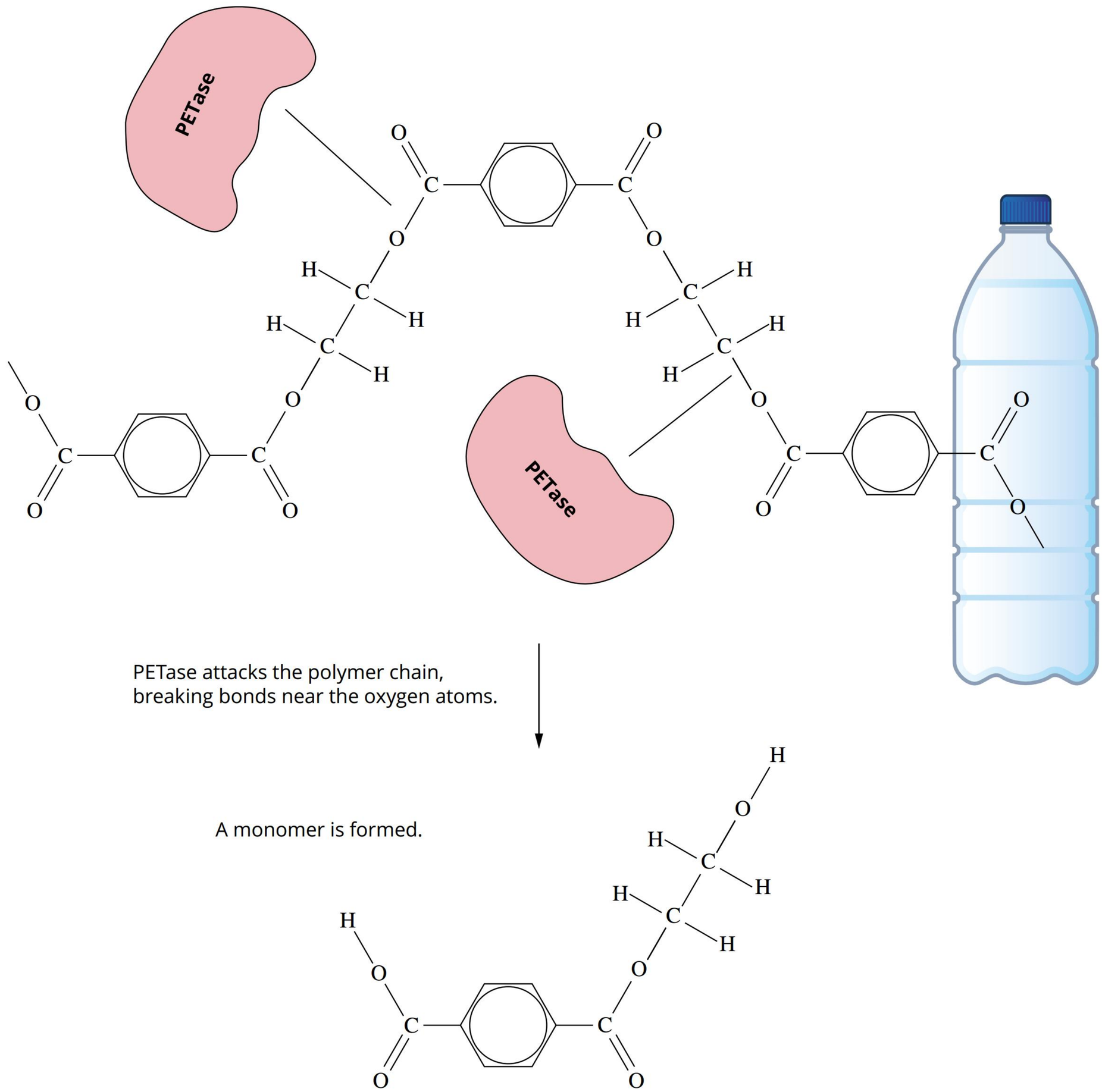


FIGURE 10.5.15 PETase enzyme can break the bonds that join the monomers in PET polymer. The enzyme has the potential to solve any problems with PET disposal contributing to landfill.

The breaking of bonds in a condensation polymer chain is referred to as **hydrolysis** (Figure 10.5.16), as water molecules released when the polymer is formed are consumed when the polymer breaks down. We see from this reversible reaction that hydrolysis, and therefore biodegradation, is likely to occur faster in aquatic environments in the presence of water.

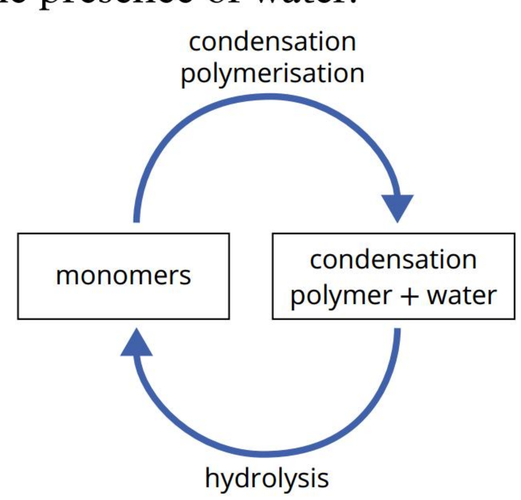


FIGURE 10.5.16 Condensation reactions can form polymers, while hydrolysis reactions break the polymers back to the monomer.

Figure 10.5.17 shows that addition polymers are less likely to biodegrade/compost than condensation polymers as the polymer backbone is entirely composed of carbon-to-carbon covalent bonds. It is the natural polymers and synthetic condensation polymers that contain oxygen atoms that are susceptible to microbial activity. In the case of PLA, the high percentage of oxygen atoms in the chain makes it a very biodegradable polymer. The rate of degradation of PLA is evident with the bottle shown in Figure 10.5.18.

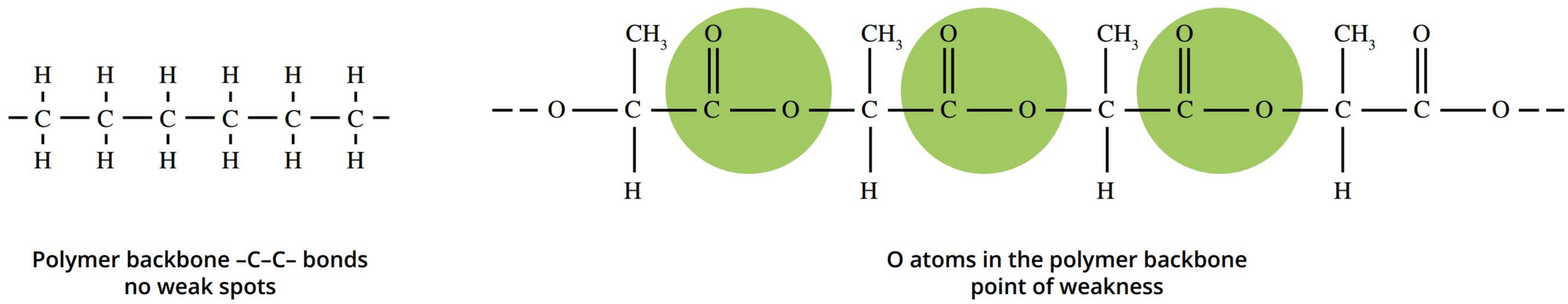


FIGURE 10.5.17 A polymer is more likely to be compostable if the backbone of the molecule contains oxygen or nitrogen atoms.

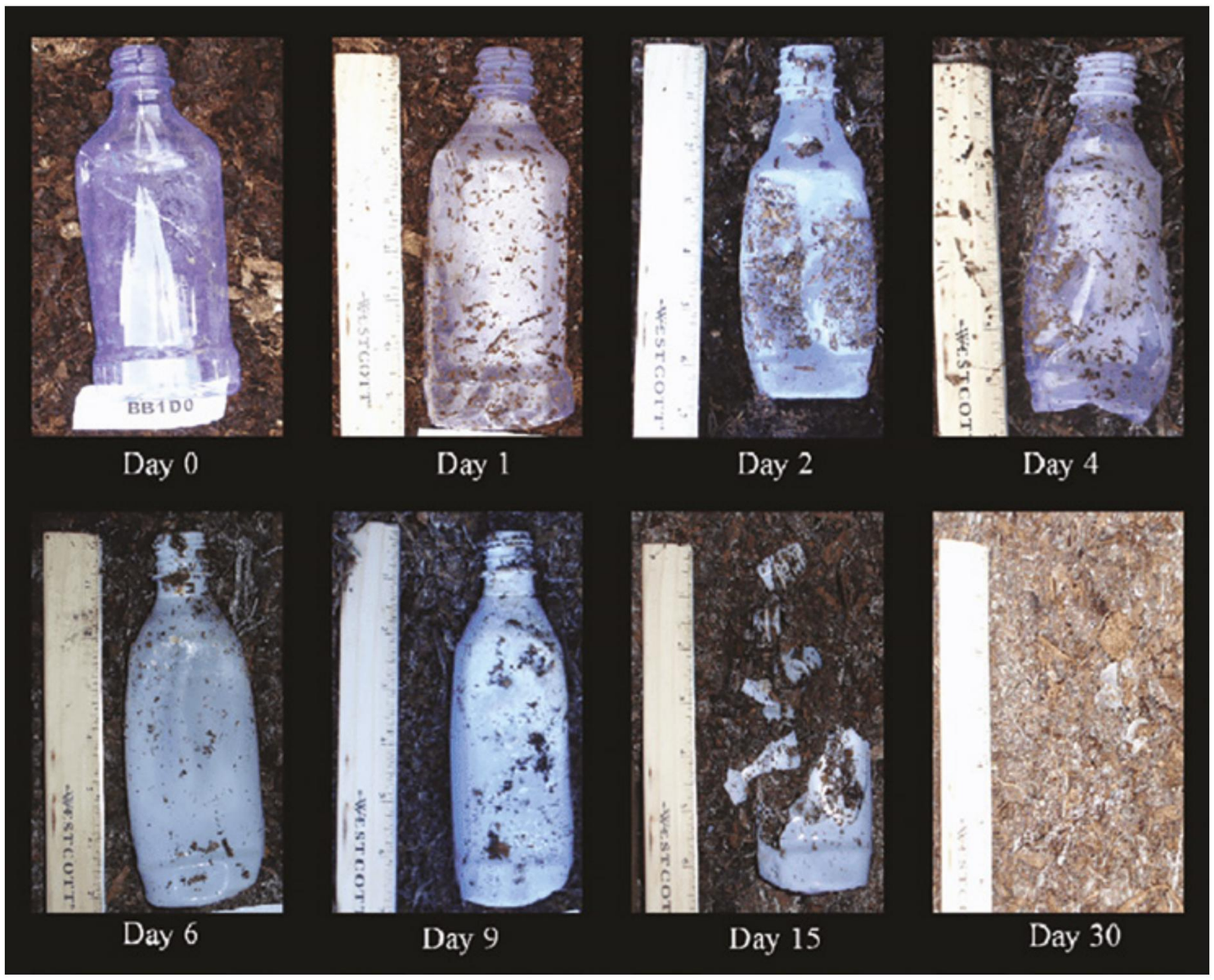


FIGURE 10.5.18 Degradation of a PLA bottle

Another benefit of PLA use is that the lactic acid monomer can be manufactured from food industry waste. Therefore, the production of PLA has a low impact on the environment, not just its disposal. This is an example of a **circular economy**, where neither the production nor disposal of a product impacts the environment. The lactic acid is produced by bacteria from waste, polymerised to PLA, which composts to non-toxic products.

> The use of biodegradable and compostable biobased polymers such as PLA is a genuine example of a circular economy. The monomer is formed from waste and the polymer biodegrades quickly to harmless products.

FIGURE 10.5.19 A range of compostable takeaway food containers

FIGURE 10.5.20 Polystyrene is broken down naturally in the stomachs of 'superworms'.

FIGURE 10.5.22 A food wrapper manufactured from oil formed from 30% recycled plastic

Starch is another natural polymer gaining in popularity due to its potential for a circular economy. The starch can be obtained as a by-product from food industries such as potato and corn processing. The products will biodegrade easily to form either the glucose monomer or CO_2. Figure 10.5.19 shows a selection of starch-based takeaway food containers.

The strategy of using microorganisms to break down plastics is being applied in new, creative ways to the process of biodegradation. A team of researchers at the University of Queensland has discovered that the common 'superworm', *Zophobas morio*, can eat through polystyrene, thanks to a bacterial enzyme in their gut. This is one of the first instances of successful composting of an addition polymer. The superworms shred the polystyrene in their mouths (Figure 10.5.20) and then the enzymes in their stomachs break the polystyrene down into smaller molecules. In the next stage, these small molecules are fed to further microorganisms that can convert them into bioplastics.

Recycling plastics

If a polymer cannot biodegrade, it is at least beneficial if it can be recycled or broken down chemically. Reprocessing involves shredding, melting and reshaping used plastic into new, clean products, as shown in Figure 10.5.21. This method can be used only with thermoplastic polymers. For example, reprocessed polyethene can be used for manufacturing plastic bags, rubbish bins and bottle crates.

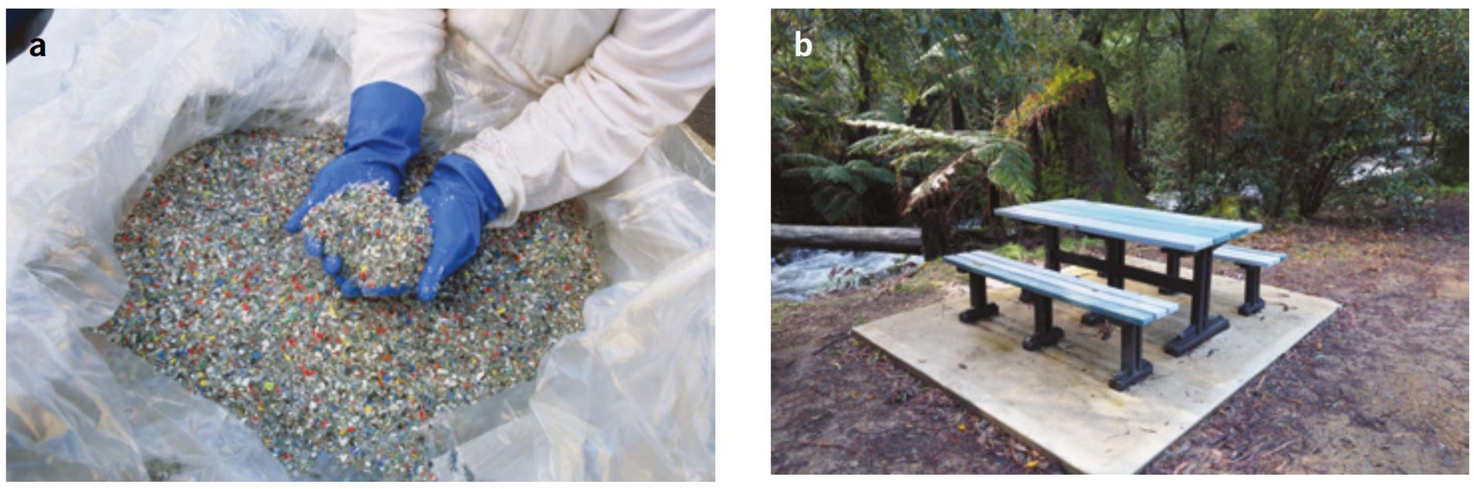


FIGURE 10.5.21 Reprocessing plastic by shredding to pellets and moulding new products

The KitKat wrapper shown in Figure 10.5.22, although just a prototype, represents an Australian 'first'—the first-time recycled plastic has been used to manufacture a food-safe polymer. The company Licella is running a trial plant in New South Wales that is using plastic waste as its feedstock. Using a combination of high temperature steam and catalysts, Licella is breaking down plastics to form a synthetic, renewable oil with similar properties and uses to crude oil. Monomers such as propene can then be formed from this oil and used to make plastics such as the chocolate wrapper shown. The Licella process is an example of chemical recycling, where the polymer structure is changed in the recycling process.

10.5 Review

SUMMARY

- Materials composed of polymers offer an almost limitless variety of properties, enabling them to be used for many different purposes.
- Factors that affect the physical properties (such as density and melting point) of polymers include the:
  - presence of cross-links
  - polarity of side groups in the polymer
  - polymer chain length
  - extent of branching of polymer chains, e.g. LDPE and HDPE
  - arrangement of side groups in the polymer chain.
- A polymer is thermoplastic if it will soften when heated, allowing it to be reshaped. A thermoplastic polymer can be recycled. Thermoplastic materials have no covalent bonds between polymer chains.
- Some polymers have covalent bonds, or cross-links, between polymer chains. Such thermosetting materials do not melt and they cannot be reshaped. If they cannot be reshaped, recycling is limited.
- The properties of a polymer are related to the packing between the polymer chains and the intermolecular forces between them. The more tightly packed polymer chains will have higher intermolecular forces.
- As most synthetic polymers are non-biodegradable addition polymers made from non-renewable resources, they pose an environmental risk.
- The term compostable has been introduced to identify polymers that are biodegradable in a reasonable time frame.
- Condensation polymers with nitrogen or oxygen atoms in the molecule backbone are more likely to be biodegradable than polymers with only carbon atoms in the molecule backbone (addition polymers).

KEY QUESTIONS

Describe

1 State one example of
- **a** an addition polymer
- **b** a natural polymer
- **c** a synthetic condensation polymer.

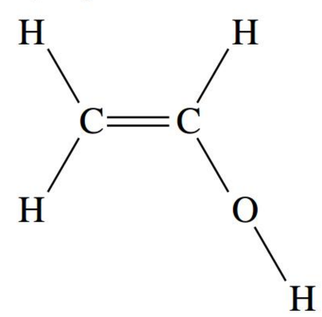
2 State three factors that influence the melting point of a polymer.

3 There are two main types of bonding present in a sample of polyethene.
- **a** Name the types of bonding present in the sample.
- **b** Which type of bond is disrupted when the polymer melts?

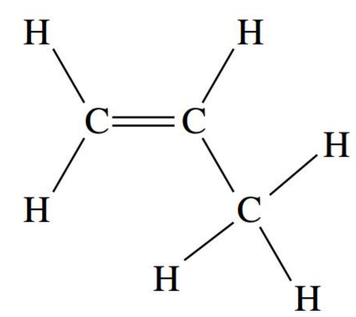
Apply

4
- **a** Use diagrams to explain the difference in structure between a thermoplastic and a thermosetting polymer.
- **b** Explain how the presence of cross-links impacts the properties of a polymer.
- **c** The majority of plastic items are made from thermoplastic polymers.
  - **i** State one disadvantage of the use of thermosetting polymers.
  - **ii** State one reason a thermosetting polymer might be used for a particular application.

5 The molecules below are both monomers for addition polymers.



monomer A



monomer B

The melting point of the polymer formed from monomer A is higher than that of the polymer formed from monomer B (assuming a similar chain length). Explain why.

6
- **a** Distinguish between a biodegradable polymer and a compostable polymer.
- **b** State a common structural feature of biodegradable polymers.

Analyse

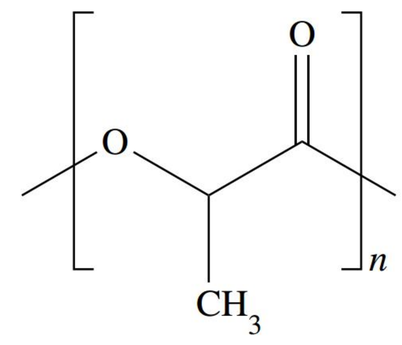
7 Modern takeaway containers are often made from starch.
- **a** List two categories of polymers that starch belongs to.
- **b** Explain why starch is readily biodegradable.
- **c** Suggest a sustainable source of starch.
- **d** Name the monomer used in starch.
- **e** Where does the polymerisation reaction take place?

Continued over page

10.5 Review *continued*

8 A brochure from a plastics manufacturer advertises several forms of polyethene. The listed melting points of these products range from 105°C to 122°C. Discuss reasons for the melting point of items made from the same monomer might vary to this degree. Include diagrams in your response.

9 Explain how the biodegradability of polylactic acid (PLA) is related to its structure.



Chapter review

10

KEY TERMS

2-amino acid
active site
addition polymer
addition reaction
aldose
amino acid
amylopectin
amylose
atactic
biodegradable
carbohydrate
cellulose
circular economy
complementary protein
compostable
condensation polymerisation
condensation reaction
copolymer
dipeptide
dipolar ion
disaccharide
elastomer
endothermic
enzyme–substrate complex
essential amino acid
ether bond
glucose
glycogen
glycosidic bond
high-density polyethene (HDPE)
hydrolysis
isoelectric point
isotactic
ketose
low-density polyethene (LDPE)
metabolised
monosaccharide
peptide link
plastic
polymerisation
polypeptide
polysaccharide
primary structure
protein
R group
recyclable plastic
side chain
starch
substrate
syntactic
thermoplastic
thermoset
tripeptide
Ziegler–Natta catalyst
zwitterion

KEY QUESTIONS

Describe

1 Select the correct statement about amino acids.
- **A** Amino acids contain only the elements C, H, O and N.
- **B** Amino acids may contain more than one nitrogen atom.
- **C** The functional group on an amino acid side chain is always non-polar.
- **D** All 20 amino acids needed by humans are known as essential amino acids.

2 A molecule of the amino acid glycine is found to have formed a positive ion. It is likely that the glycine
- **A** has formed a zwitterion.
- **B** is in alkaline conditions.
- **C** is in acidic conditions.
- **D** has been heated.

3 Eisenin is a tripeptide. It is formed in
- **A** a condensation reaction between three amino acids.
- **B** an addition reaction between three amino acids.
- **C** a condensation reaction between amino acids and water.
- **D** an addition reaction between amino acids and water.

4 Starch and cellulose are both formed from the
- **A** polymerisation of glycine.
- **B** polymerisation of two different monosaccharides.
- **C** reactions between different functional groups on each end of a monomer.
- **D** polymerisation of glucose.

5 Identify the description that best describes a polymer.
- **A** a very long covalent molecule constructed from a repeating unit
- **B** a very long molecule with no pattern to its structure
- **C** a giant lattice of atoms in a repeating pattern
- **D** a very long molecule

6 Identify the statement that best describes HDPE as compared to LDPE. HPDE contains:
- **A** cross-links that lead to a lower melting point.
- **B** much longer molecules with stronger covalent bonds.
- **C** more polar molecules resulting in a higher boiling point.
- **D** fewer branches in the chains resulting in a higher melting point.

7 A particular reaction is found to form two peptide linkages and to release two molecules of water. The reaction could be

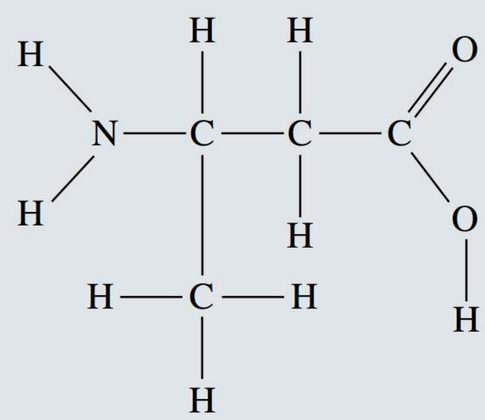
A a condensation reaction to form a dipeptide.
B a condensation reaction to form a tripeptide.
C an addition reaction to form a dipeptide.
D an addition reaction to form a tripeptide.

8 The molecular formula of a compound is $C_{12}H_{22}O_{11}$. It is likely that the compound is

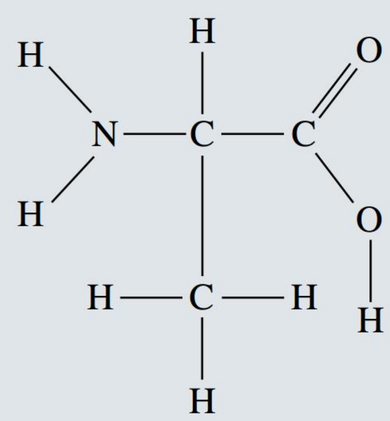
A an amino acid.
B a disaccharide.
C a polymer formed from glucose.
D a dipeptide.

9 One of the molecules below is a 2-amino acid.

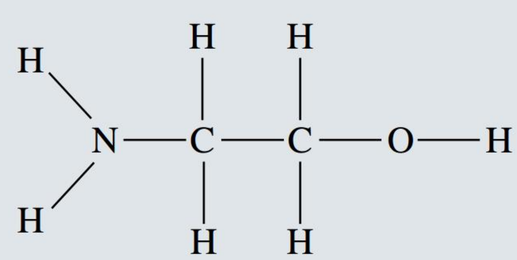
A



B



C



Identify the 2-amino acid and explain why the other two molecules are not 2-amino acids.

10 Describe the primary structure of a protein.

11 Name the functional groups that react to form the following:

a a glycosidic link
b a peptide link
c an ester bond.

12 Draw the general structure of a 2-amino acid. Label the functional groups.

Apply

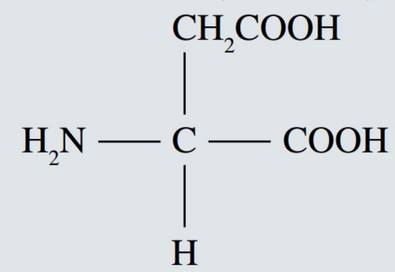
13 Define the following terms:

a 2-amino acid
b dipeptide
c condensation reaction
d monomer.

14 Draw structural formulas of the two dipeptides that can be formed from the reaction between alanine and serine.

15 Write a balanced chemical equation for the reaction between two molecules of glycine.

16 Aspartic acid, drawn below, is one of the non-essential amino acids. It exists mainly as a zwitterion at its isoelectric point of pH 2.8.



a Name the:

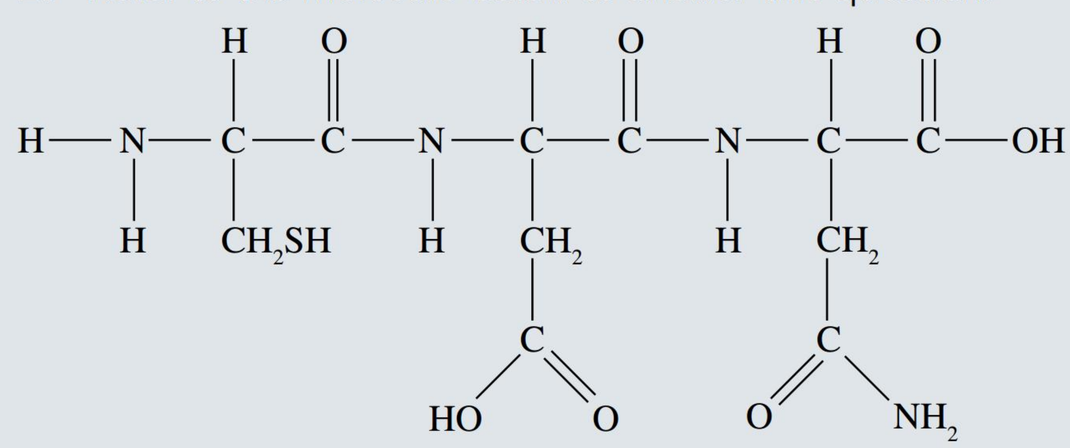
i acidic functional group
ii basic functional group.

b Explain what is meant by the term 'zwitterion'.

c Draw the structure of the molecule as it is most likely to exist in a solution at:

i pH much greater than 2.8
ii pH much less than 2.8
iii pH 2.8.

17 Refer to the molecule below to answer this question.



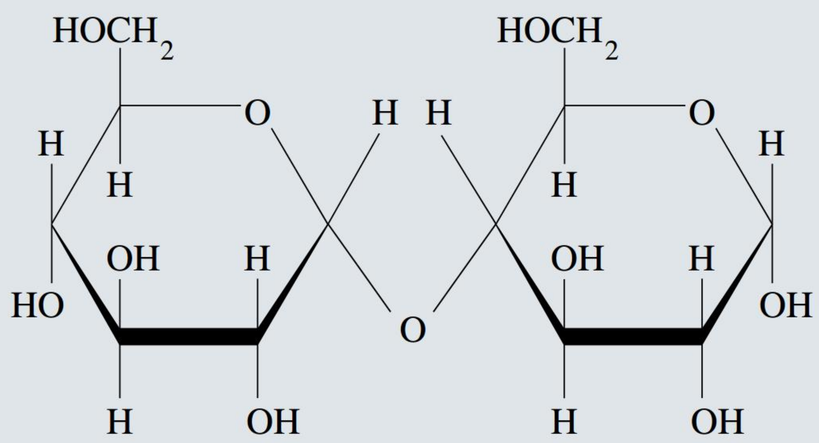
a Circle the peptide links in this molecule.

b Identify the amino acids used to form this molecule.

c Use amino acid shorthand to describe this molecule.

d How many water molecules were released in the condensation reaction that formed this molecule?

18 The structure below is that of maltose, a molecule found in wheat and other cereals.



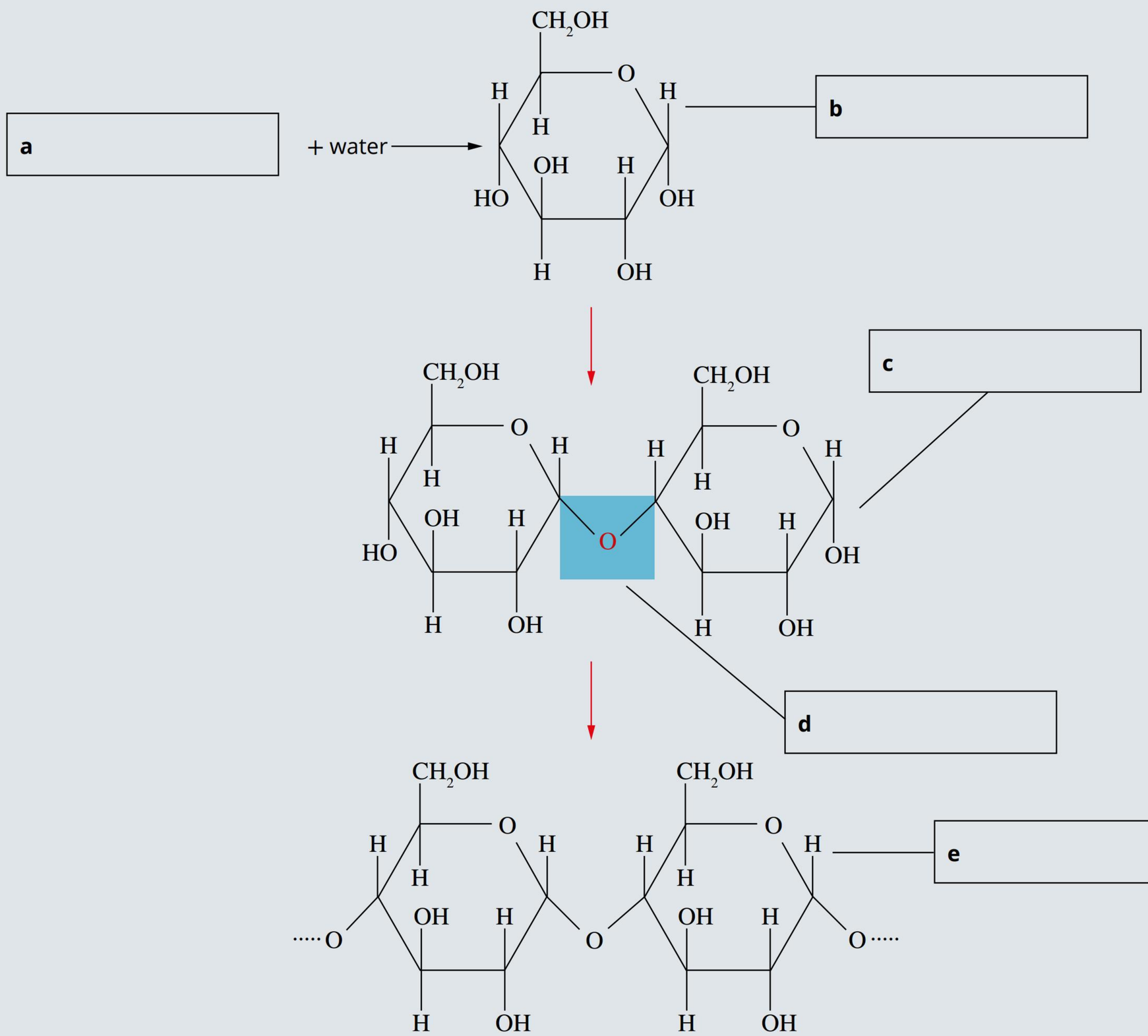
a Refer to the structure of maltose to explain what a disaccharide is.

b Circle and name the linkage between the two molecules.

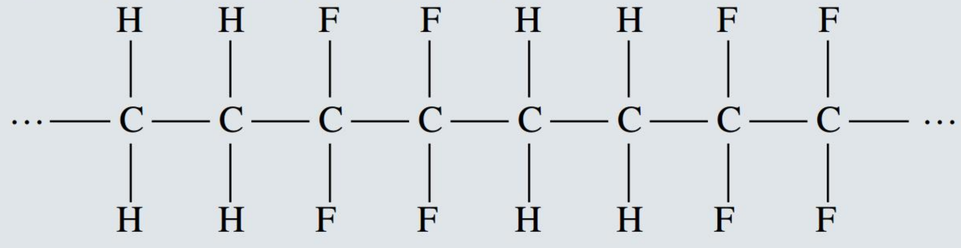
c Describe how maltose is formed from smaller molecules.

19 Use the following terms to complete labels **a**–**e** in the diagram below, which shows the formation of a polysaccharide.

polysaccharide, disaccharide, carbon dioxide, glycosidic link, glucose



20 Determine the number of different monomers required to form this polymer. Provide the condensed structural formula for the two monomers.

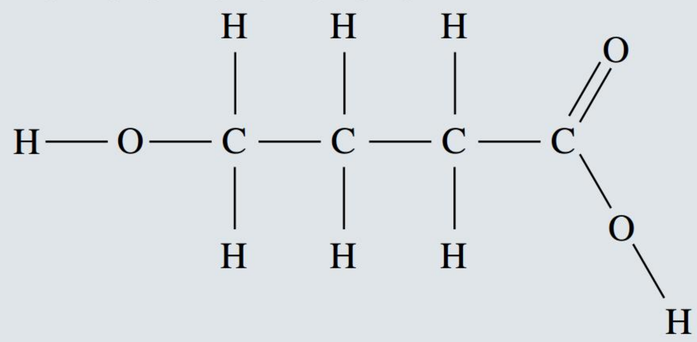


21 Explain the following terms using polyethene as an example.

a addition polymerisation

b unsaturated and saturated

22 **a** Draw a section of the polymer that could be formed from the monomer shown.

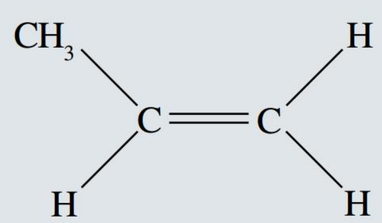


b Use the structure you have drawn to explain what a condensation polymer is.

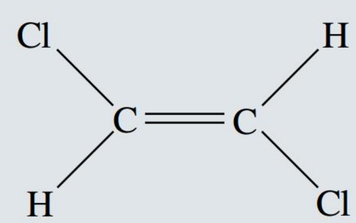
c The polymer formed is an example of a biodegradable polymer. Identify the structural feature of this molecule that leads to its biodegradability and describe the attribute that would make it also compostable.

23 Draw a section of the polymers formed from each of the following monomers.

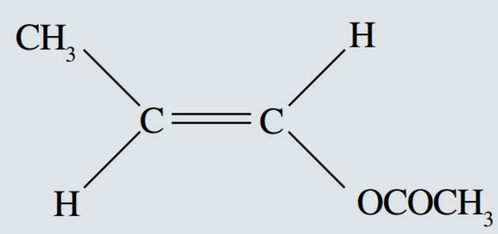
a



b



c



Analyse

24 Enzyme activity is influenced by changes in pH. Changing pH can alter the charge on some functional groups because they act as weak acids or bases. The R groups of a polypeptide chain are important in maintaining the enzyme's tertiary structure. Complete the following table for each of the R groups listed.

Structure of R group	Is the R group acidic or basic or neither?	Is the R group positively charged, negatively charged or neutral?	
		In a solution of pH 2	In a solution of pH 11
$-CH_2COOH$			
$-CH_2CH(CH_3)_2$			
$-CH_2OH$			
$-(CH_2)_4NH_2$			

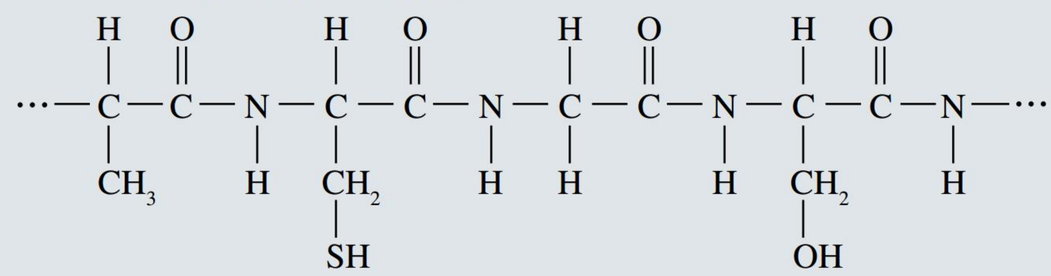
25 When alanine and glycine (Table 10.1.1 on page 400) react, two different dipeptides can be formed.

a Provide the condensed structural formula of each dipeptide.

b Determine the number of tripeptides that can be formed from three amino acids (assuming each amino acid is only used once).

c Proteins are formed using 20 different amino acids and can be hundreds of amino acid units in length. On the basis of your answers to parts **a** and **b**, state a conclusion about the number of different proteins possible.

d Show the peptide links in the section of a protein chain shown below.



e Provide condensed structural formulas for the amino acids that make up this section of the chain.

26 Identify the strongest type of intermolecular force present between polymer molecules produced from the following monomers.

a ethene ($CH_2{=}CH_2$)

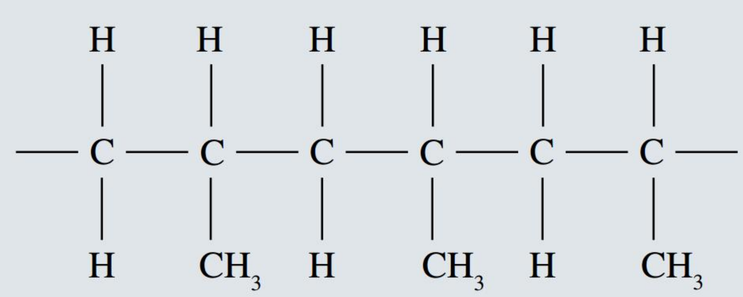
b vinyl chloride ($CH_2{=}CHCl$)

c styrene ($CH_2{=}CHC_6H_5$)

d propene ($CH_2{=}CHCH_3$)

e acrylonitrile ($CH_2{=}CHCN$)

27 A typical section of a polymer is shown below.



a Name the term used to describe the arrangement of the side groups in the polymer.

b Draw the monomer from which this polymer is produced.

c Identify the number of repeating monomer units shown.

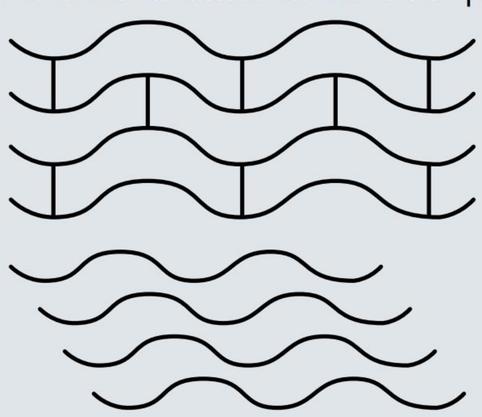
Interpret

28 If the amino acids alanine (Ala) and cysteine (Cys) are mixed and reacted in condensation reactions, a mixture of products forms.

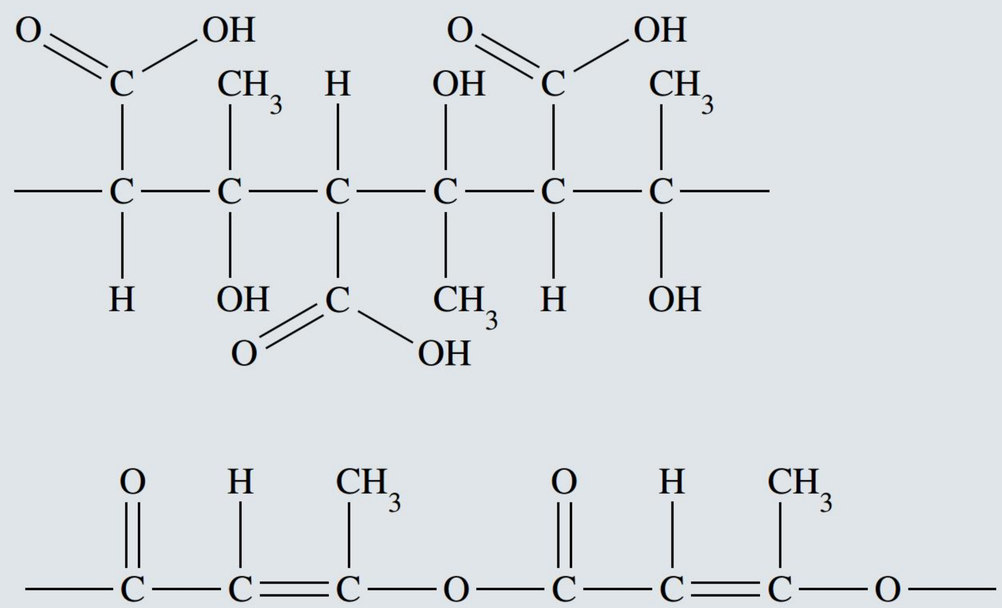
a When the products are isolated and analysed, four different dipeptides are identified. Use shorthand amino acid notation to list the four products.

b Use shorthand notation to determine the number of different tripeptides that could form from alanine and cysteine.

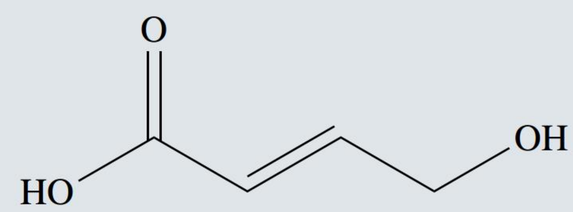
29 Refer to the two models shown to discuss the structural differences between thermoplastic and thermosetting polymers. Your response should link structural differences with property differences.



30 **a** Determine which of the following monomers, labelled **A**–**C**, could be used to produce both of the polymer chains shown below.



A



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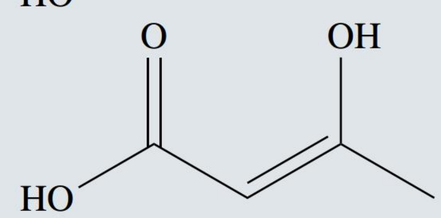
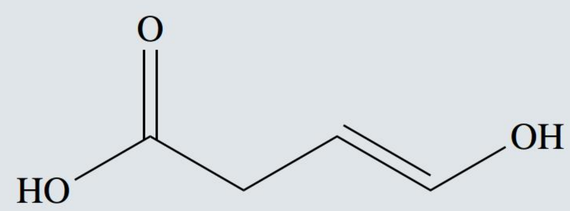
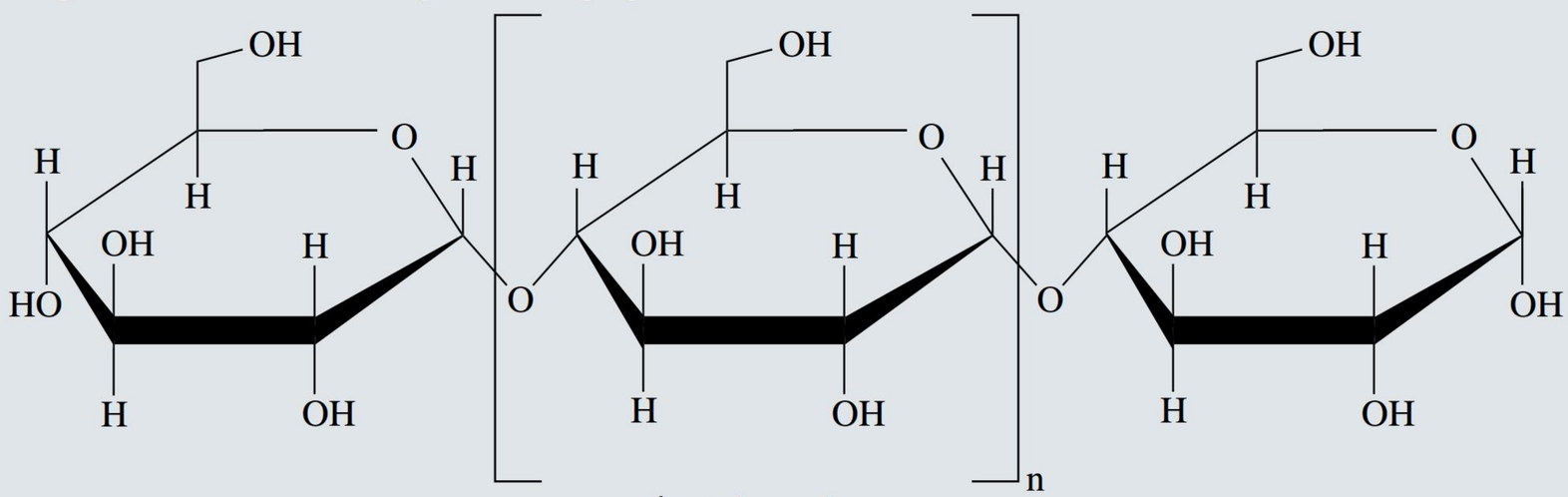


C



b Justify why the remaining monomers would not be applicable.

31 The diagram shows the general structure of a dextrin. Dextrins are short-chain polysaccharides formed during the digestion of starch. They have highly branched structures.



dextrin unit

Explain what you can deduce about the chemistry of dextrins from the diagram and the brief introduction. Your response should consider the categories this substance belongs to and its likely properties.

Data analysis

DATA SET 1

The information below relates to Questions 1–5.

The first commercial synthetic polymers were made early in the last century. At that time, scientists had little control over the reactions and the lengths of the polymer molecules, and the degree of branching varied significantly. Since then, scientists have developed a range of complex catalysts that allow greater control over the polymerisation process.

The table below shows some of the properties of samples of polyethene available from a supplier. The first column of the table shows the average molecule length (in terms of the number of monomer units used) of polymers in each sample.

Number of ethene monomers in polymer	Melting point (°C)	Density (kg/m^3)	Tensile strength (MPa)
1000	110	910	10
2000	115	916	14
5000	127	934	21
10 000	135	961	38
50 000	141	968	48
100 000	147	975	62

Question 1 (2 marks)

a Draw the monomer ethene.

b Draw a segment of the polymer polyethene.

Question 2 (4 marks)

a Plot a graph to represent the relationship between melting point and molecule length.

b Describe any trend evident in your graph.

Question 3 (2 marks)

Question **2** focused on melting point. Discuss the data provided for density and tensile strength. Does it follow the same overall trend as the melting point?

Question 4 (2 marks)

Refer to the polymer structure to explain why the properties are changing in the patterns shown.

Question 5 (3 marks)

A toy manufacturer chooses to use isotactic polypropene instead of polyethene for a range of bats for a ball sport. Discuss some of the considerations the manufacturer might have used when selecting the more expensive polypropene.

CHAPTER 11

Analysis of organic compounds

In Units 1 and 2, you were introduced to instrumental methods of chemical analysis such as chromatography, mass spectrometry and atomic absorption spectroscopy. These methods are based on the chemical and physical properties of substances, and help analytical chemists to determine how much of a substance is present in a sample.

The properties of substances can also be used to determine their identity. Analytical chemists combine knowledge of the properties of chemicals with instrumental methods to identify and quantify substances. Analytical instruments coupled with computers are extremely accurate and are able to detect and identify very small amounts of complex substances.

In this chapter, you will learn about four instrumental techniques used to identify and determine the structure of organic compounds—chromatography, electrophoresis, mass spectrometry and infrared spectroscopy. You will also analyse data from these techniques to identify an organic compound, including empirical, structural and molecular formula. Percentage composition can also be determined from this information (Figure 11.0.1).

FIGURE 11.0.1 Identification of unknown substances is essential for forensics.

Syllabus subject matter

Topic 1 • Properties and structure of organic materials

ANALYTICAL TECHNIQUES

- Explain how amino acids can be separated and identified by paper chromatography/TLC, including intermolecular forces/solubility in mobile and stationary phases and retention (R_f) values. **11.1**
- Explain how amino acids can be separated and analysed by electrophoresis, including pH of buffer, isoelectric points and movement of charged ions. **11.2**
- Analyse data, including paper/TLC chromatograms and electrophoresis, to determine the identity of amino acids and retention factors. (Formula: $R_f = \frac{\text{distance moved by the amino acid}}{\text{distance moved by the solvent}}$) **11.1 and 11.2**
- Analyse data from spectra, including mass spectroscopy and infrared, to determine the identity and structure of organic molecules. **11.3–11.5**
- Analyse data to determine the structural, molecular and empirical formula of organic compounds and the percentage composition of elements in organic compounds. **11.3 and 11.5**

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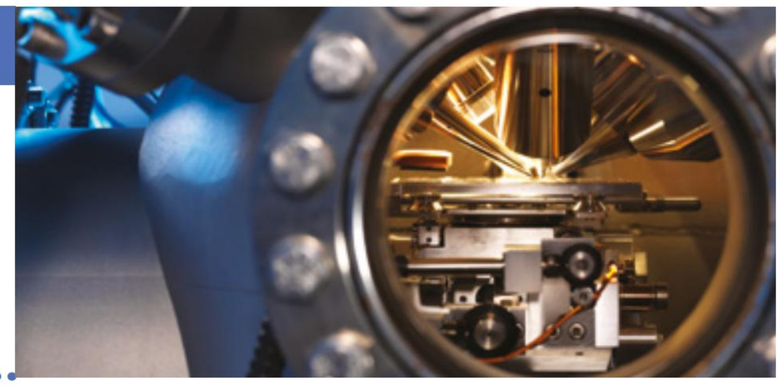
11.1 Chromatography

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand how amino acid mixtures can be separated in chromatography
- predict the polarity of the 20 natural amino acids based on their –R groups
- calculate the R_f values from the paper and TLC chromatographs
- identify amino acids from R_f values.



In Unit 2, you learnt about the principles of chromatography and how it is a widely used technique for separating and analysing complex mixtures of organic compounds. Food, petrochemicals, perfumes and pharmaceuticals are all mixtures that can be separated by chromatography. This section describes the use of paper chromatography and **thin-layer chromatography (TLC)** to separate and identify amino acids.

REVISION

Chromatography is a technique to separate out **components** in a mixture.

Mobile phase (the moving phase) can be in either a liquid or gas state and can be a polar or non-polar substance.

Stationary phase (the non-moving phase) can be in either a solid or a liquid state.

The components in the mobile phase flow over or through the stationary phase, undergoing a continual process of **adsorption** (onto the stationary phase), followed by **desorption** and dissolving (into the mobile phase).

The rate of movement of each component mainly depends on how strongly the component adsorbs onto the stationary phase and how readily the component dissolves in the mobile phase.

The components separate because they undergo adsorption and desorption at different rates due to their different **polarities**.

Paper chromatography uses high-quality absorbent paper as the stationary phase.

TLC uses a thin layer of fine powder, such as alumina (aluminium oxide) or silica gel, spread thin on a glass or plastic plate as the stationary phase.

When the mixture separates out onto the paper or TLC plate, the pattern of bands or spots is called a **chromatogram**.

Both paper chromatography and TLC are useful for **qualitative analysis**. They can indicate which chemicals are present in the mixture but cannot give their specific concentration.

Colourless compounds on the chromatograph must be made visible using ultraviolet light or spray with a chemical that reacts to the compound to form a coloured spot.

> The term 'adsorption' describes the adhesion of molecules or substances to the surface of a solid or liquid. This is why the stationary phase in chromatography is either a solid or a liquid. The mobile phase is in either a liquid or a gas state.

AMINO ACIDS

You learnt about amino acids in Module 10.1. This section investigates the separation and identification of these amino acids using paper chromatography or TLC. Separation of the different amino acids requires knowledge of the polarity of the –R group off the α-carbon, as highlighted in Figure 11.1.1. Table 11.1.1 lists the 20 amino acids' –R groups and their polarities, categorised into non-polar, polar and charged at pH 7 (either as negative or positively charged). Recall, polar and charged molecules will readily dissolve in water, whereas non-polar molecules will not. For simplicity, the charged –R groups will be grouped with polar –R groups as both dissolve in water.

The Senior Chemistry Formula and Data Book does not categorise the amino acids into their respective polarities. Instead, you will use your past knowledge of electronegativity and chemical structure to recognise the polarity and/or charge of the –R group. The following guidelines will assist in determining the polarity or charge:

1. The –R groups that have only carbon and hydrogen bonds, such as Ala and Leu, will be non-polar.
2. The –R groups that contain oxygen or nitrogen will all be polar/charged (depending on pH) except tryptophan (see step 3).
3. Tryptophan –R group contains a nitrogen, but it is classified as non-polar due to the relatively large double-ring structure.
4. The amino acids that contain sulfur in the –R group are cysteine and methionine.
   - Cysteine is categorised as polar as the sulfur is more electronegative than hydrogen, making the –SH group polar.
   - Methionine is categorised as non-polar as the carbon and sulfur have the same electronegativity.

The –R groups that are charged at pH 7 form the strongest intermolecular forces with water (ion–dipole forces).

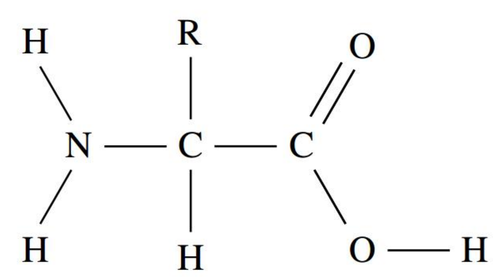
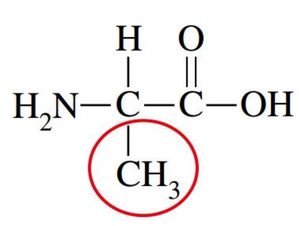
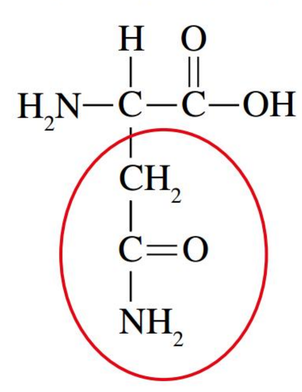
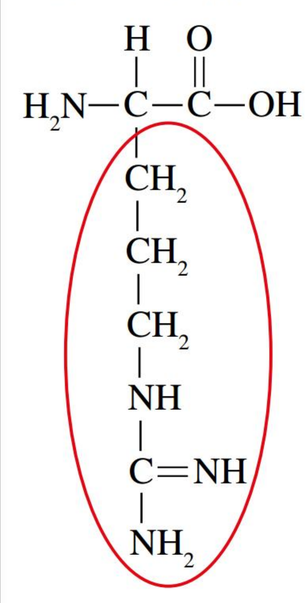
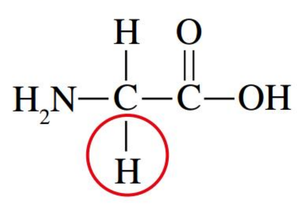
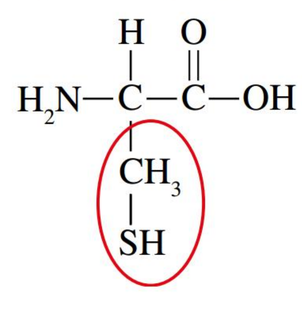
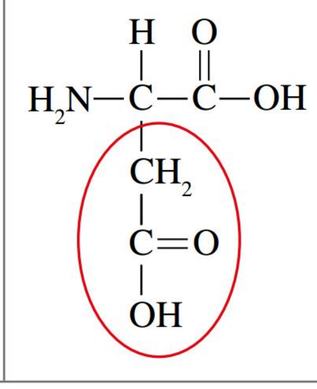
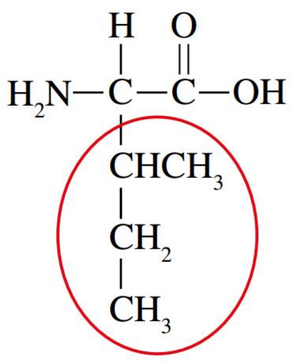
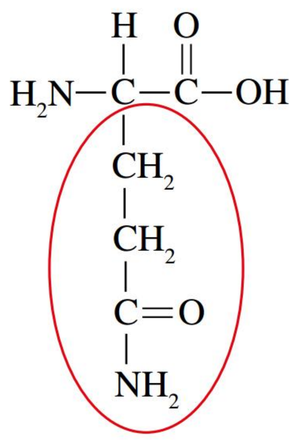
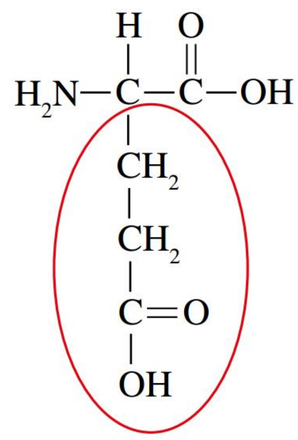
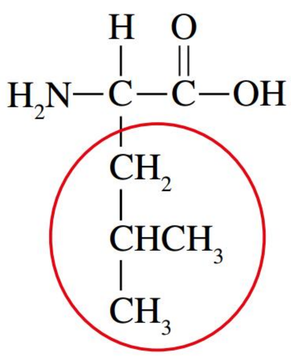
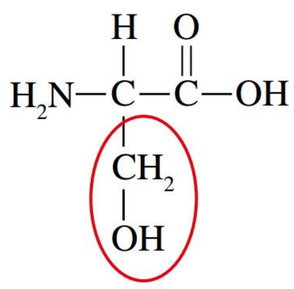
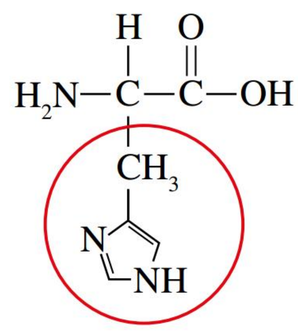
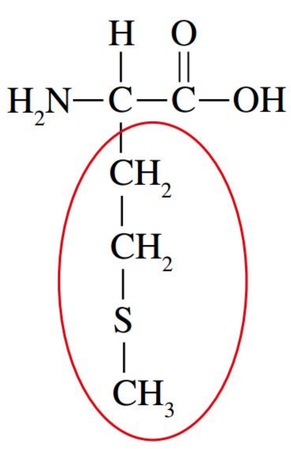
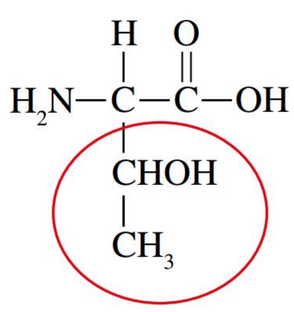
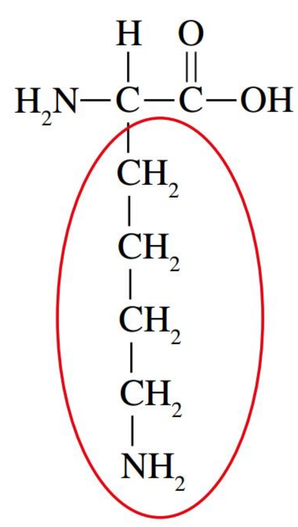
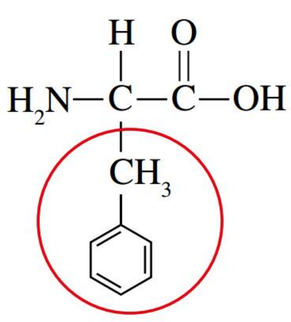
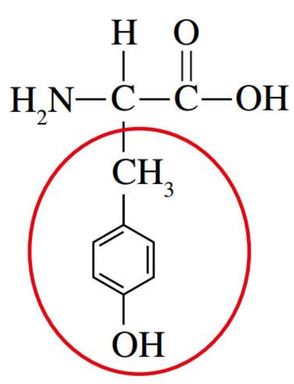
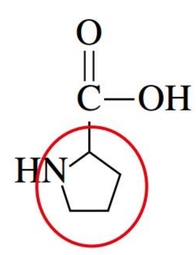
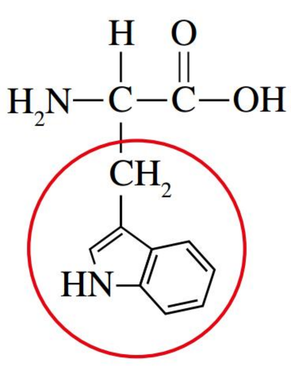
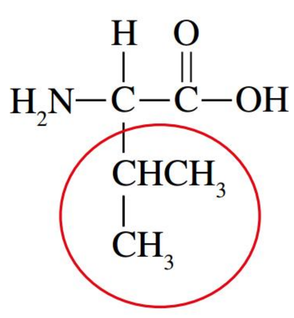


FIGURE 11.1.1 The general structural formula of an amino acid with the –R group highlighted. The –R group determines the polarity of the amino acid.

TABLE 11.1.1 The –R groups of the 20 naturally occurring amino acids and their polarities categorised into non-polar, polar and (positive and negative) charged at pH = 7 (very polar). The –R group is highlighted in red.

Non-polar	Polar	–R group has a (+) or (–) charge at pH 7 (polar)
Alanine (Ala) 	Asparagine (Asn) 	Arginine (Arg) 
Glycine (Gly) 	Cysteine (Cys) 	Aspartic acid (Asp) 

Isoleucine (Ile) 	Glutamine (Gln) 	Glutamic acid (Glu) 
Leucine (Leu) 	Serine (Ser) 	Histidine (His) 
Methionine (Met) 	Threonine (Thr) 	Lysine (Lys) 
Phenylalanine (Phe) 	Tyrosine (Tyr) 	Proline (Pro) 
Tryptophan (Try) 	Valine (Val) 	

MOBILE AND STATIONARY PHASE POLARITIES

The stationary phase for paper chromatography is primarily cellulose, which forms a polar surface of –OH groups. The stationary phase for TLC is also polar. Therefore, to separate out amino acids in mixtures successfully, the polarity of the mobile phase is very important. The mobile phase could be anywhere between 100% non-polar (e.g. hexane) to 100% polar (water). However, 100% non-polar or 100% polar mobile phases are never used as some amino acids would not be able to dissolve in such a solvent. The ideal choice of polarity for the mobile phase must:

- completely dissolve all the different amino acids in the mixture
- maximise the separation of the amino acids on the chromatograph.

SEPARATION OF AMINO ACIDS

Separation of amino acids in paper and thin-layer chromatography relies upon the intermolecular forces between the amino acids and the stationary and mobile phases. The three intermolecular forces, dispersion forces, dipole–dipole attractions and hydrogen bonding, determine how far the amino acid will travel on the stationary phase, depending on the solvents used in the mobile phase.

Hydrogen bonding is the strongest intermolecular force. Mobile phase solvents containing carboxylic acid, alcohol groups or water are able to form hydrogen bonds with carboxylic acid, hydroxyl or amino groups within the –R group. For example, ethanoic acid can form hydrogen bonds with the aspartic acid –R group ($–CH_2COOH$).

Alcohol-based solvents are an example of a solvent that is also able to form dipole–dipole attractions to the polar –R groups. As such, solvents such as butan-1-ol can form dipole–dipole attractions with amino acids such as cysteine.

Solvents commonly used in separating amino acids using paper or thin-layer chromatography include the mixture of butan-1-ol and concentrated ethanoic acid or the mixture of 0.5 M ammonium hydroxide and propan-2-ol. These solvents are less polar than water, are able to dissolve all 20 amino acids and can separate the mixtures effectively.

The polarity of the mobile phase dictates the relative distance travelled on the paper or TLC plate. The more polar mobile phases allow the polar and charged –R group amino acids to travel the furthest along the plate. The non-polar –R group amino acids prefer not to remain in the solvent and adsorb strongly onto the stationary phase, generally staying at or close to the origin position.

The more soluble the amino acid is in the mobile phase, the further it will travel up the paper or TLC plate.

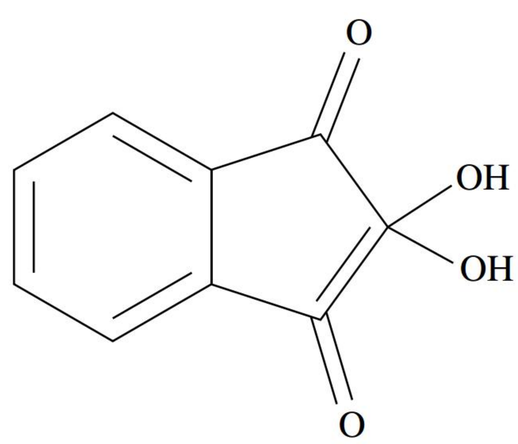


FIGURE 11.1.2 The structural formula of ninhydrin

DETECTING THE AMINO ACIDS

Amino acids are colourless. To observe them on the paper or TLC plate, a chemical called ninhydrin (Figure 11.1.2) is used. Ninhydrin is a chemical that reacts with amino acids to form a colour. Depending on the amino acid, these colours range from purple, yellow, pink or grey. Note, you cannot identify the amino acid from the colour, as many amino acids form the same colour.

In the laboratory, ninhydrin is sprayed onto the paper or TLC plate after the separation process is complete and the solvent has dried. The resulting chromatogram can then be analysed to identify the amino acids (Figure 11.1.3).

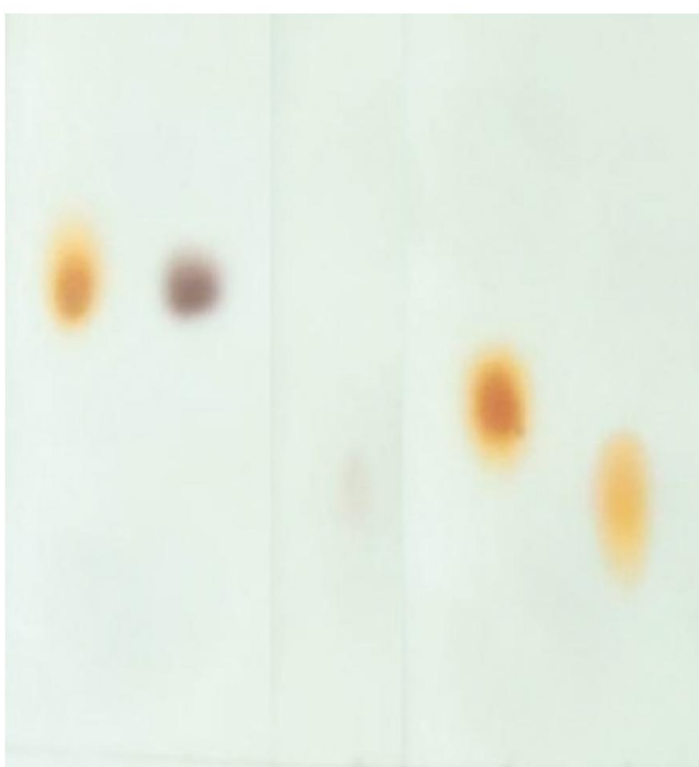


FIGURE 11.1.3 Amino acids separated using silica thin-layer chromatography. The amino acids are colourless and their positions have been revealed using the ninhydrin stain.

Identifying amino acids on chromatograms

The amino acids in a mixture can be identified by including standards of known amino acids on the same chromatogram as the unknown sample or calculating the **retardation factor (R_f)** of the amino acid. The identity of the amino acid can be determined by using R_f tables. It is very important, when comparing the R_f table with your data, that the conditions of the experiment are identical, especially the mobile phase solvents you used. Different solvents mean different polarities, which means different intermolecular forces dictate the distance the amino acid travels. For example, tryptophan has a different R_f value when a more polar mobile phase

(0.50) is used compared to a less polar mobile phase (0.77). Refer to Skillbuilder below for the calculation of R_f.

Using known standards

Suppose you wish to find out whether an unknown sample (sample X) contains the amino acids serine and lysine. You place sample X on the same chromatogram as a pure sample of each of serine and lysine (the 'standards'). If spots from sample X move the same distance from the origin as the spots from the pure samples, then sample X is likely to contain the amino acids, as shown in Figure 11.1.4.

For this method, the sample and standards are 'run' on the same chromatogram because the distances moved from the origin will depend on the solvent used as the mobile phase and the distance moved by the **solvent front**. The further the solvent front is allowed to travel, the further the spots travel.

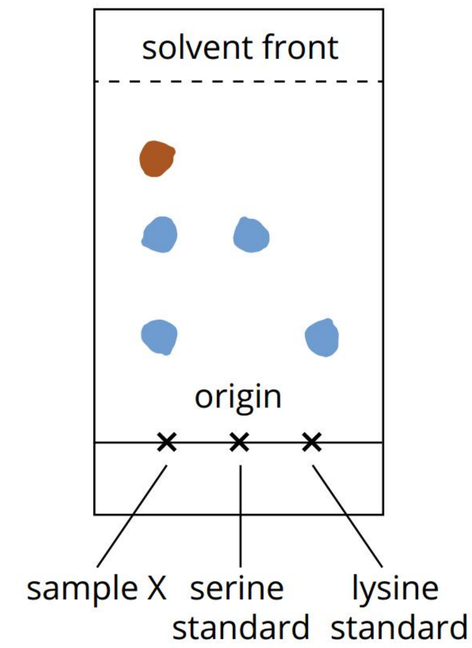


FIGURE 11.1.4 Identification of amino acids serine and lysine in an unknown sample (sample X) using paper or thin-layer chromatography. Sample X is likely to contain serine and lysine, as well as a brown-coloured component.

> 'Solvent front' is the term used to describe the movement of the solvent during chromatography. It is visible as the wet moving edge of the solvent as it travels along the stationary phase.

SKILLBUILDER

Calculating R_f values

The retardation factor (R_f) for a component can be used to identify the components of a mixture by calculating the distance they travel up the stationary phase compared to the distance travelled by the solvent front. This is expressed as a retardation factor (R_f) for a component:

$$R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$$

The R_f values are always less than one, which means that the component most strongly adsorbed onto the stationary phase moves the shortest distance and has the lowest R_f value.

Each component has a characteristic R_f value for the conditions under which the chromatogram was obtained. By comparing the R_f values of components of a particular mixture with the R_f values of known substances determined under identical conditions, you can identify the components present in a mixture.

This means the R_f values of unknown spots can be compared against a table of R_f values of common materials. Using Figure 11.1.5, calculate the R_f value of the blue and red components.

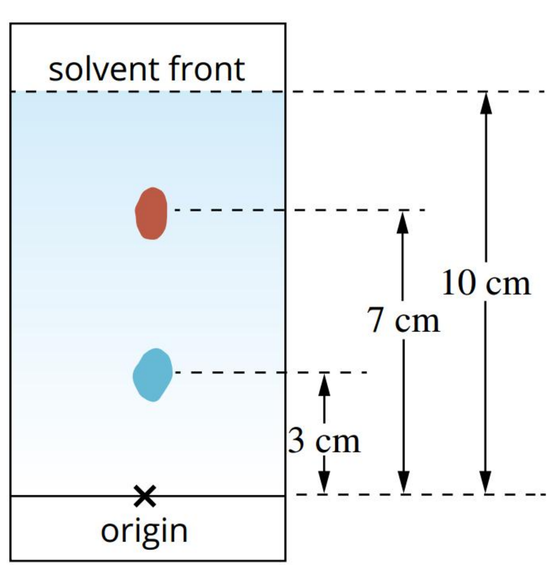


FIGURE 11.1.5 A thin-layer chromatogram of a sample with two components. The distances from the origin enable you to calculate R_f.

Step 1: Record the distance the component has moved from the origin and the distance the solvent front has moved from the origin.

- The distance the solvent front has moved from the origin is 10 cm.
- The distance the blue component has moved from the origin is 3 cm.
- The distance the red component has moved from the origin is 7 cm.

Step 2: Calculate the R_f value of the blue component using the following formula:

$$R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$$

$$R_f(\text{blue component}) = \frac{3}{10} = 0.3$$

$$R_f(\text{red component}) = \frac{7}{10} = 0.7$$

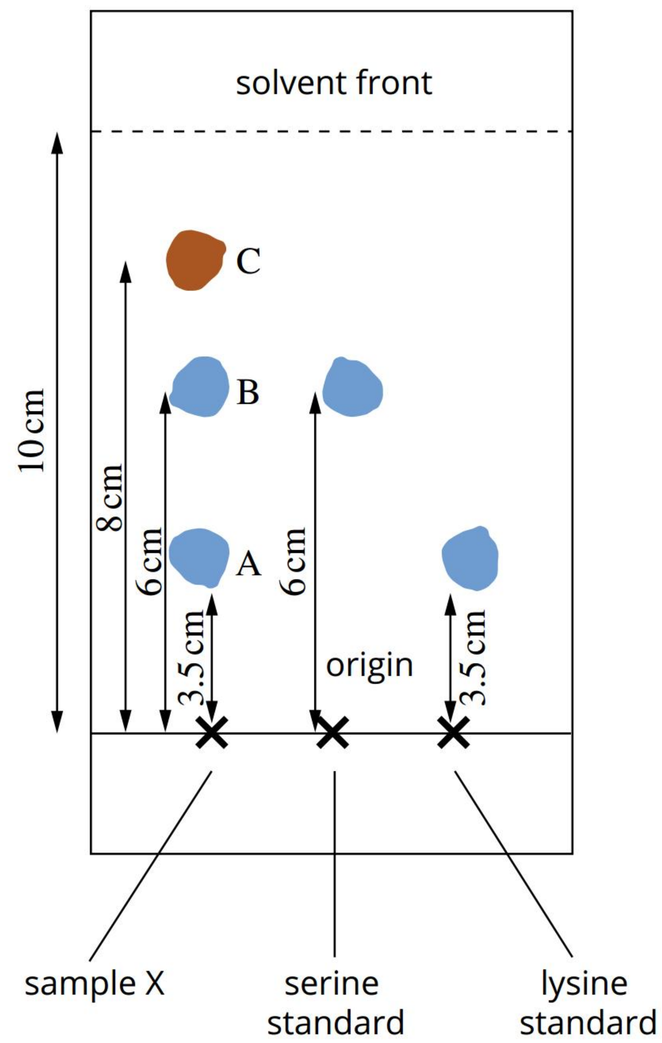
Step 3: Compare the R_f values of unknown substances with the R_f values of common materials and identify the components.

For the R_f value of a component to be comparable to a set of standard R_f values, the experiment must be conducted under identical conditions.

Worked example 11.1.1

CALCULATING R_f VALUES

Using the following figure, calculate the R_f values of the different components of sample X. Using qualitative and quantitative data, show that sample X contains lysine.



Thinking	Working
Record the distance component A has moved from the origin, the distance the lysine sample has moved from the origin and the distance the solvent front has moved from the origin.	The distance that component A has moved from the origin is 3.5 cm. The distance the lysine sample has moved from the origin is 3.5 cm. The distance the solvent front has moved from the origin is 10 cm.
Calculate the R_f value of the lysine sample and component A using the following formula: $R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$	$R_f(\text{lysine}) = \frac{3.5}{10}$ $= 0.35$ $R_f(\text{component A}) = \frac{3.5}{10}$ $= 0.35$
Compare the R_f values of unknown substances with the R_f values of common materials and identify the components.	Sample X's component A and lysine both travelled up the chromatograph the same distance and the calculated R_f values were the same. Thus, sample X does contain lysine.

➤ Try yourself 11.1.1

CALCULATING R_f VALUES

Using the figure in Worked example 11.1.1, calculate the R_f values of the different components of sample X. Using qualitative and quantitative data, show that sample X contains serine.

Using R_f values

As stated above, it is possible to identify amino acids using a data set of R_f values, so long as all the experimental conditions are identical. It is essential that the solvent used in the mobile phase is identical. If a different solvent is used, the mobile phase will have a different polarity. The intermolecular forces between the mobile phase and the amino acids will be different, and so the distance these amino acids travel up the plate will be different. As shown in Worked example 11.1.1, the distance each amino acid travels up the plate determines the R_f value.

Typical R_f data sets will look like Table 11.1.2. The mobile phase solvents are provided, and volumes are given as a ratio. For example, in mobile phase 1, you will make up the solvent mixture as 6 mL of butan-1-ol, 3 mL of ethanoic acid and 1 mL of water. Notice that the R_f values can be identical for some amino acids. Aspartic acid and glycine both have an R_f value of 0.26 for mobile phase 1. As the two amino acids have the same value, it will be impossible to identify an unknown with an R_f value of 0.26. It would be best to use another mobile phase with a different polarity to separate these two amino acids successfully. Using mobile phase 2 gives an R_f for aspartic acid as 0.40 and glycine as 0.50, so repeating the chromatography with mobile phase 2 solvents will successfully identify these two amino acids.

TABLE 11.1.2 A typical data set of R_f values for five amino acids in two different mobile phases using TLC

Amino acid	R_f value in mobile phase 1 butan-1-ol + ethanoic acid + water (60:30:10)	R_f value in mobile phase 2 butan-1-ol + propan-2-one + ethanoic acid + water (40:40:5:5)
alanine	0.31	0.46
asparagine	0.12	0.45
aspartic acid	0.26	0.50
glycine	0.26	0.40
leucine	0.72	0.75

11.1 Review

SUMMARY

- Chromatography is a technique to separate out and identify compounds in a mixture based on the polarity of the compounds and their intermolecular forces between the stationary and mobile phases.
- The mobile phase must have the ideal polarity to be able to dissolve all the components in the mixture as well as maximise the separation on the stationary phase.
- Amino acids in a mixture can be separated and identified by paper and thin-layer chromatography.
- Separation occurs due to the polarities of the–R group on the amino acid.
- The polarity of the –R group on the amino acid is determined by the electronegativities and chemical structure.
- The amino acids of a mixture separate during chromatography as a consequence of how strongly they adsorb to the stationary phase and desorb back into the mobile phase, based on the intermolecular forces.
- Paper and thin-layer chromatography can be used to identify amino acids in a mixture by comparing them with known standards or by determining their R_f values.
- R_f data sets can be used to identify amino acids, but the exact experimental conditions must be adhered to, especially the solvents used in the mobile phase.

KEY QUESTIONS

Describe

1 Write out the formula to calculate the R_f value.

2 Identify the stationary phase for each of the following:

a paper chromatography

b thin-layer chromatography.

Apply

3 List one reason why you must not touch the surface of the TLC plate before an experiment to separate out amino acids.

4 A thin-layer chromatogram shows one component at the top of the plate, and one close to the bottom (near the origin). Explain what this tells you about the rate of adsorption and desorption of the two components.

5 Explain why ninhydrin is part of the experimental process to identify amino acids using paper chromatography.

6 One way to identify amino acids on a chromatogram is to use known standards. Explain how this method identifies an unknown amino acid on a chromatogram.

7 Name the two factors required for the ideal mobile phase used to separate out amino acids.

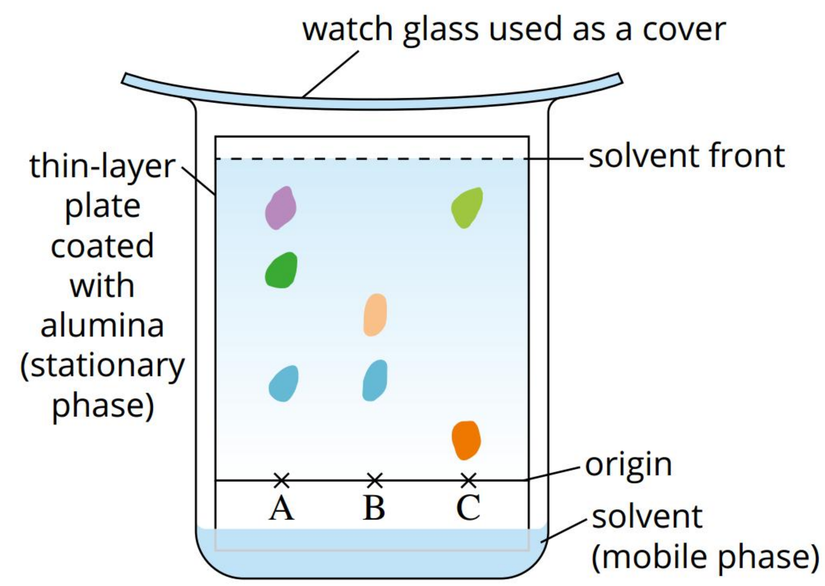
Analyse

8 An amino acid has a straight carbon chain –R group.
   a Classify the amino acid as polar or non-polar.
   b If a more polar mobile phase is used in the TLC setup, predict the distance travelled on the plate. Explain your reasoning.

9 A mixture contains the amino acid molecules serine, threonine and valine. Predict the relative distance travelled for each amino acid up a TLC plate if a polar mobile phase is used.

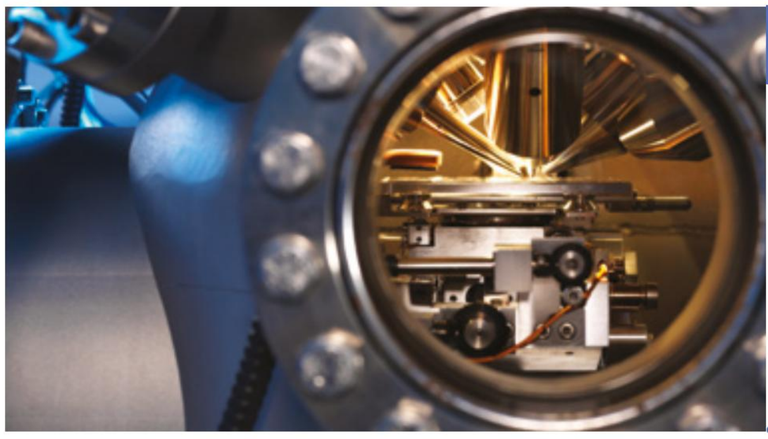
10 **a** Consider the diagram below showing a thin-layer chromatogram of three different samples (A, B and C), and:
   i determine how many different components are present in sample B
   ii select which colour of sample A is least strongly adsorbed on the stationary phase
   iii show which samples are likely to have one component in common.

   b The green spot in sample A is 8.0 cm above the origin. The R_f value of this green spot is 0.74. The orange and green spots of sample C are 3.0 cm and 9.0 cm above the origin, respectively. Calculate the R_f values of each component of sample C. Give your answer to two decimal places.



11 The following materials are commonly used in chromatography: water, ethanol, glass sheets, paper strips, powdered alumina, nitrogen gas and hexane. Choose a suitable stationary phase and polar mobile phase from the list to use in the analysis of amino acids by thin-layer chromatography.

11.2 Electrophoresis



BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- explain the use of electrophoresis for amino acid separation and analysis
- outline the principles of electrophoresis
- explain the role of pH in the buffer solution to form charged amino acids
- identify amino acids based on pH, isoelectric points and the movement of the charged amino acids.

Electrophoresis is a technique used for separating proteins, amino acids and nucleic acids (DNA and RNA). Many organic molecules carry a net charge and will migrate at a rate proportional to their charge. When an electric current is applied to the gel, the negatively charged molecules in the gel move towards the positive terminal and the positively charged molecules in the gel move towards the negative terminal.

PRINCIPLES OF ELECTROPHORESIS

Amino acids are **amphoteric** and can therefore carry a charge depending on the pH of the environment. An amphoteric compound can act as an acid or a base, by donating or accepting hydrogen ions.

Electrophoresis of amino acids can be undertaken using either gel or paper. The gel used has a jelly-like texture and is usually a **polyacrylamide gel (PAGE)**. High-quality, finely textured paper is used for paper electrophoresis. The paper and gel consist of a three-dimensional network of solid material and pores, which aid the movement of amino acid molecules.

Amino acids are separated according to their overall charge, whether it is positive, negative or neutral, at a particular pH.

Ninhydrin is added to the paper or gel after analysis so that the separated amino acids are visible.

A high-voltage battery is used to force a current through the gel or paper. The battery is attached to the negative and positive terminals of the paper or gel, and a buffer solution is added that conducts electricity. After loading a number of separate amino acid samples in a line along the centre of the gel/paper, the positively charged amino acids will travel to the negative terminal, while the negatively charged amino acids will travel to the positive terminal. The neutral amino acids will remain stationary.

In electrophoresis, the negative terminal is the cathode and the positive terminal is the anode.

The electrode names for electrophoresis are similar to electrolysis, where the negative terminal is the cathode and the positive terminal is the anode.

The following steps outline the process of gel electrophoresis that is represented in Figure 11.2.1.

1. The electrophoresis gel is prepared. The gel is rectangular and contains small wells (holes) in a row in the centre.
2. The gel is placed into a gel electrophoresis chamber with the wells situated at the centre of the chamber.
3. Each sample is loaded into one of the wells within the gel.
4. The gel is placed in an electrophoresis bath where it is covered with a controlled pH solution (buffer) that contains ions to conduct an electric current.
5. A power source is attached to the electrophoresis bath and switched on. The electrical current causes the negatively charged amino acids to migrate through the gel towards the positive terminal of the chamber. The positively charged amino acids migrate through the gel towards the negative terminal.
6. Any neutral amino acids remain stationary in the centre wells.
7. The colourless amino acids are detected by spraying ninhydrin on the gel and allowing it to dry.

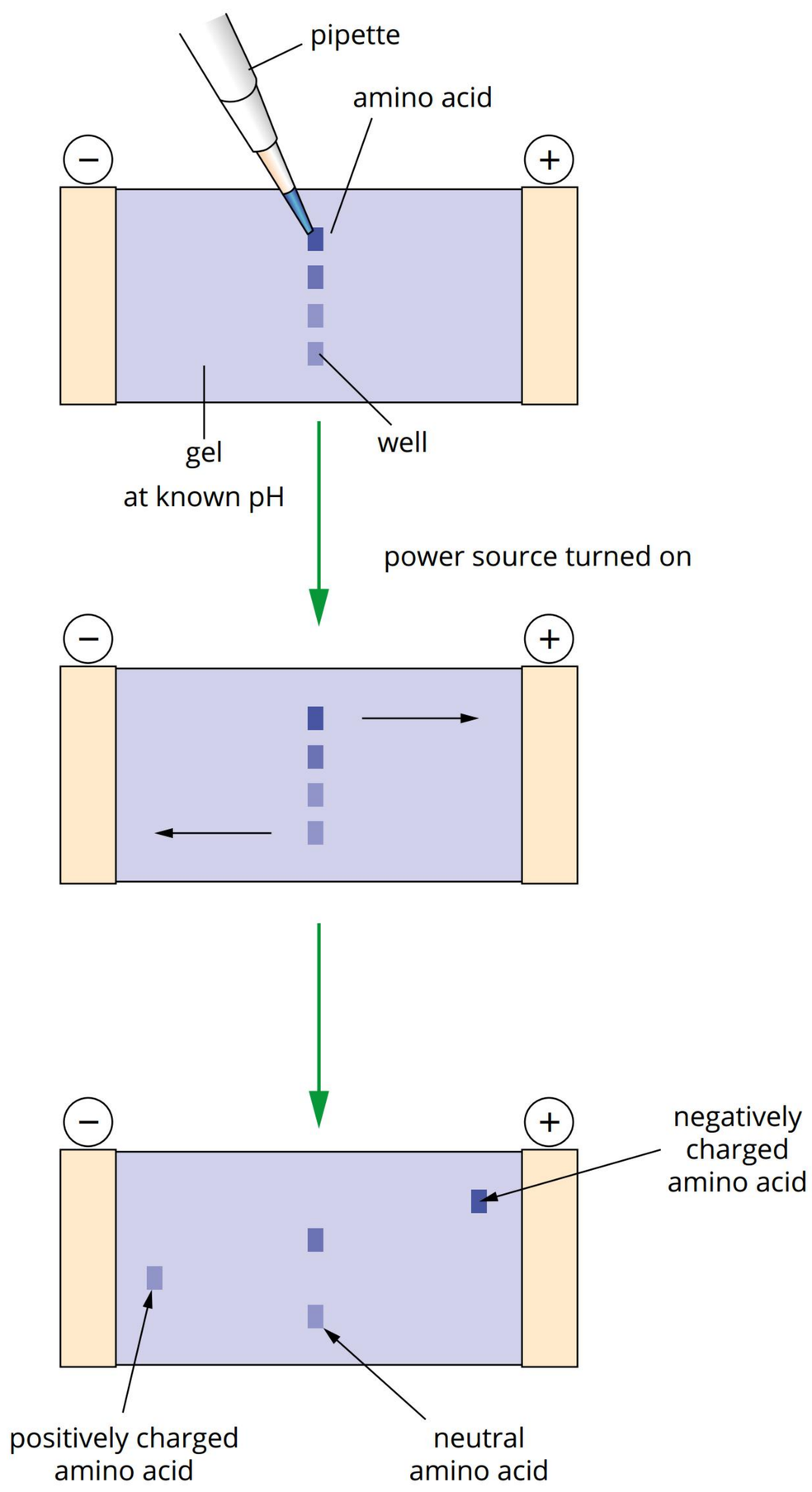


FIGURE 11.2.1 The process of gel electrophoresis, showing three different amino acids being loaded into wells and migration of the amino acids to the terminals based on their charge.

The following steps outline the process of paper electrophoresis:

1. The paper is placed onto a flat platform with its edges submerged in buffer solution. The paper must be saturated with the buffer.
2. Each sample is loaded onto the centre of the paper as a spot.
3. The terminals are attached to opposite edges of the paper.
4. A power source is attached and switched on. The electrical current causes the negatively charged amino acids to migrate through the saturated paper towards the positive terminal of the chamber. The positively charged amino acids migrate through the saturated paper towards the negative terminal.
5. Any neutral amino acids remain stationary in the centre.
6. The colourless amino acids are detected by spraying ninhydrin on the paper and allowing it to dry.

ISOELECTRIC POINTS

In Module 10.1, you learnt about amino acids as zwitterions and the formation of cations and anions based on the pH of the solution. In this module, we will expand on this topic to explain how changing the pH of the solution can assist in identifying amino acids.

Each amino acid forms a zwitterion at a known pH value. This pH value is known as the **isoelectric point**, and it is a very important value to know for separating amino acids using electrophoresis. Table 11.2.1 lists these values, and they are also provided for you in the Senior Chemistry Formula and Data Book. Just like other weak acids and bases, amino acids will ionise to differing degrees. The exact pH at which they form a neutral molecule will therefore vary. Most amino acids have isoelectric points between 5.0 and 6.5. These isoelectric points are slightly acidic as the carboxylic acid on the α-carbon is a slightly stronger acid than the amine group is as a base.

If the amino acid has acidic or basic –R groups, the isoelectric values will fall outside this range. The amino acids with basic –R groups (amino groups) tend to have isoelectric points above 8, as you need basic conditions to deprotonate one of the amine groups on the –R group to form a neutral molecule. Similarly, the amino acids with acidic –R groups (carboxyl groups) have isoelectric points below 5, as acidic conditions are required to protonate one of the carboxylic acid groups to form a neutral molecule.

TABLE 11.2.1 The pH of isoelectric points for the 20 amino acids

Amino acid	pH of isoelectric point	Amino acid	pH of isoelectric point
aspartic acid	3.0	tryptophan	5.9
glutamic acid	3.2	leucine	6.0
cysteine	5.1	isoleucine	6.0
asparagine	5.4	valine	6.0
threonine	5.6	glycine	6.1
tyrosine	5.7	alanine	6.1
glutamine	5.7	proline	6.3
serine	5.7	histidine	7.6
methionine	5.7	lysine	9.7
phenylalanine	5.7	arginine	10.7

When an amino acid undergoes electrophoresis at the pH of its isoelectric point, that amino acid has an overall neutral charge and does not migrate to the electrodes. It will remain in the centre of the paper or gel. If the pH of the buffer is less than the isoelectric point, the amino acid has an overall positive charge. It will migrate to the negatively charged electrode. Likewise, if the pH of the buffer is greater than the isoelectric point, the amino acid has an overall negative charge. It will migrate to the positively charged electrode. Figure 11.2.2 shows a simplified diagram of these key points. Note that all amino acids will become charged at certain pHs.

All charged amino acids will migrate at different rates, depending on the isoelectric point and the pH of the buffer. Recall, weak acids form an equilibrium reaction with water, and the equilibrium constants, K_a, and the resulting pK_a values determine the isoelectric point. The rate of migration to the electrode is based on the proportion of the amino acid which is charged at the pH of the buffer. Basically, the larger the difference between the isoelectric point and the pH of the buffer, the greater the percentage of the amino acid will be charged, and so faster to migrate.

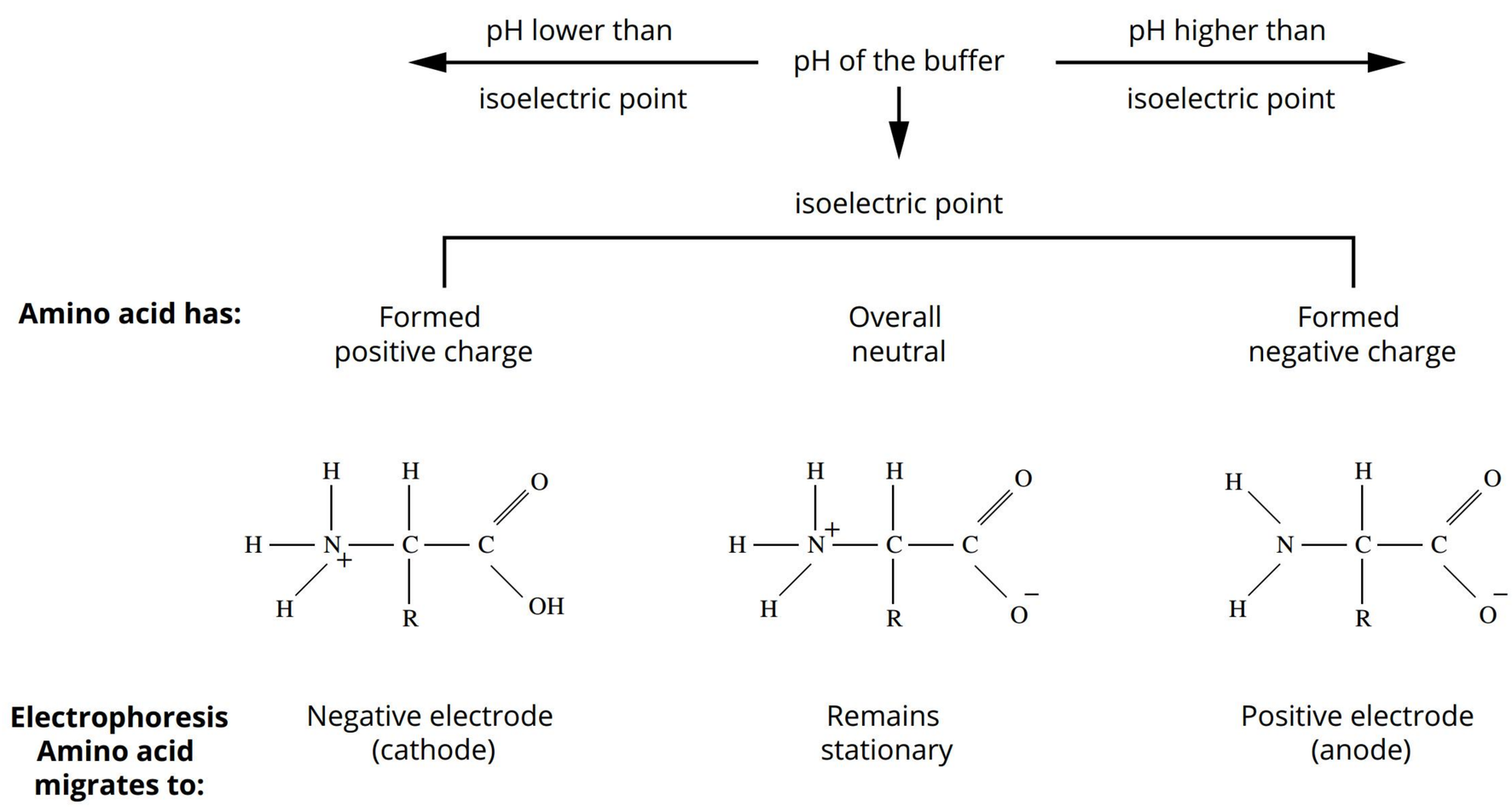


FIGURE 11.2.2 A simplified diagram to show the changes with the overall charge of amino acids and whether the amino acids migrate to the electrodes or remain stationary, depending on the pH of the buffer

Worked example 11.2.1

PREDICTING THE CHARGE OF AMINO ACIDS

Predict the charge of the following amino acids at the listed pH of buffer solutions:

a arginine at pH 7.0

b cysteine at pH 10.0

c leucine at pH 6.0.

Thinking	Working
Look up the pH of isoelectric points for the amino acids.	**a** pH of isoelectric point of arginine is 10.7 **b** pH of isoelectric point of cysteine is 5.1 **c** pH of isoelectric point of leucine is 6.0
Compare the pH of isoelectric point with the pH of the buffer solution and determine whether it is less than, greater than or equal to each other.	**a** pH of isoelectric point of arginine is 10.7 pH of buffer solution is 7.0 The pH of the buffer solution is less than the pH of isoelectric point. **b** pH of isoelectric point of cysteine is 5.1 pH of buffer solution is 10.0 The pH of the buffer solution is greater than the pH of isoelectric point. **c** pH of isoelectric point of leucine is 6.0 pH of buffer solution is 6.0 The pH of the buffer solution is equal to the pH of isoelectric point.

Determine whether the amino acid has an overall negative, positive or neutral charge at the given pH of the buffer solution.	**a** Arginine is in a buffer solution that has a pH less than its isoelectric point. Therefore, arginine will have an overall positive charge. **b** Cysteine is in a buffer solution that has a pH greater than its isoelectric point. Therefore, cysteine will have an overall negative charge. **c** Leucine is in a buffer solution that has a pH equal to its isoelectric point. Therefore, leucine will have an overall neutral charge.

➤ Try yourself 11.2.1

PREDICTING THE CHARGE OF AMINO ACIDS

Predict the charge of the following amino acids at the listed pH of buffer solutions:

a aspartic acid at pH 9.0

b glycine at pH 6.1

c phenylalanine at pH 3.5.

IDENTIFYING AMINO ACIDS USING ELECTROPHORESIS

Amino acids can be identified using electrophoresis. By changing the pH of buffer solutions to values on either side of isoelectric points and observing the presence or absence of amino acids at the cathode, anode and those that remain stationary, it is possible to identify unknown amino acids, or at least narrow down the list of possibilities.

Let's consider a mixture of four different amino acids: valine, serine, aspartic acid and lysine. A paper electrophoresis experiment is set up, and a pH buffer solution of 6.0 is used. The pH of isoelectric points for the four amino acids are listed in the brackets: valine (6.0), serine (5.7), aspartic acid (3.0) and lysine (9.7). At pH 6.0, valine will have an overall neutral charge, serine will have a slightly negative charge, aspartic acid will have an overall negative charge and lysine will have an overall positive charge. Once the electrophoresis experiment has completed, you will find an amino acid at the cathode and anode as well as two in the centre. Lysine will migrate to the negatively charged electrode, and aspartic acid will migrate to the positively charged electrode. Valine will remain stationary in the centre, and serine will have migrated slightly to the positively charged electrode. As serine has an isoelectric point of 5.7, at pH buffer of 6.0, only a small percentage of the sample will be charged. Since a small percentage of serine has a negative charge, it has migrated a small distance from the centre due to the slow migration rates.

Many amino acids have similar isoelectric points. For example, alanine and glycine both have an isoelectric point of 6.1. Similarly, methionine, phenylalanine, serine and tyrosine all have an isoelectric point of 5.7. Therefore, it is impossible to separate out these amino acids using electrophoresis.

11.2 Review

SUMMARY

- Electrophoresis is a technique that can be used to separate amino acids.
- Paper or gel can be used as the medium for amino acid separation.
- A buffer solution at a set pH is used to control the pH of the experiment and provide ions for the electrical current.
- The amino acids are placed in the centre of the gel or paper and an electric current is applied.
- Positively charged amino acids (cations) migrate to the cathode (negative electrode).
- Negatively charged amino acids (anions) migrate to the anode (positive electrode).
- Amino acids that have an overall neutral charge will remain in the centre of the paper/gel.
- The isoelectric point is the pH value where an amino acid has an overall neutral charge.
- If the pH of the buffer solution is greater than the isoelectric point, the amino acid becomes negatively charged by donating protons to the solution.
- If the pH of the buffer solution is less than the isoelectric point, the amino acid becomes positively charged by accepting protons from the solution.
- Identification of some amino acids in a mixture is possible by changing the pH of the buffer to alter the charge of the amino acids present. At a given pH, some amino acids may be negatively charged, some may be neutral and some may be positively charged.

KEY QUESTIONS

Describe

1 List the key components required for an electrophoresis experiment to separate amino acids.

2 Amino acids are amphoteric. Explain what this means.

Apply

3 Define the isoelectric point, using alanine as an example.

4 Predict the charge of tryptophan in a pH buffer solution of 9.0.

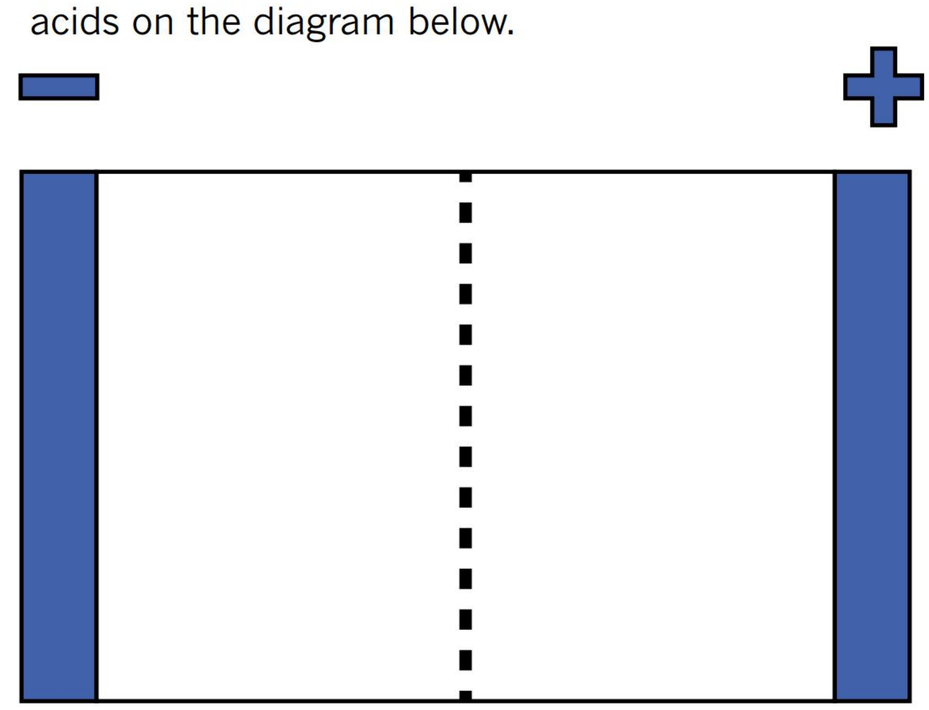
5 Explain why you can separate glutamine and glutamic acid, but you cannot separate glutamine and methionine using electrophoresis.

Analyse

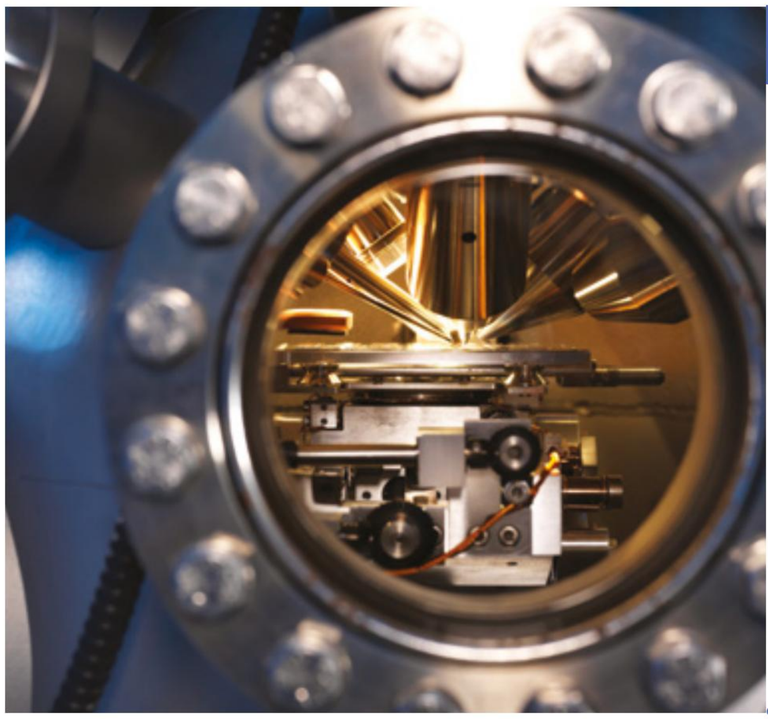
6 A student sets up an electrophoresis experiment using gel and two different pH buffer solutions: pH=2.5 and pH=5.5. Predict the locations of the following amino acids (cathode, anode or centre) in each solution.

a arginine
b cysteine
c histidine
d glutamic acid

7 An electrophoresis experiment was conducted with isoleucine, lysine and valine using a buffer solution of pH 6.0. Draw where you expect to see these amino acids on the diagram below.



11.3 Mass spectroscopy



BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- briefly outline principles of mass spectrometry
- explain the fragmentation of molecules when placed in a mass spectrometer
- identify the base peak and molecular ion on a mass spectrum
- analyse and interpret the mass spectrum of organic molecules
- use data given to interpret a mass spectrum and identify the organic molecules tested
- determine the structural formula, empirical formula and molecular formula of an organic compound based on the molecular ion seen in the mass spectrum and fragmentation pattern.

FIGURE 11.3.1 An artistic impression of Curiosity, a robotic rover, on the surface of Mars

Mass spectrometry is one of the most commonly used analytical tools. It is used to analyse samples of solids, liquids and gases. It is a very sensitive quantitative technique that can detect concentrations in the parts per billion to parts per trillion range (nanograms per kilogram).

In Unit 1, you studied the use of mass spectrometry in the analysis of isotopes of an element. Mass spectrometry can also be applied to identify an unknown compound in a sample. Each molecule produces its own unique mass spectrum (like a fingerprint), so a molecule can be identified by comparing its mass spectrum with the mass spectra held in a database.

Mass spectrometry is used to determine the structure of proteins and drugs. It can also detect molecules that are common markers for diseases such as cancer. Mass spectrometers have also been used in space exploration to analyse the atmosphere of Mars and the moons of Saturn. The Mars rover Curiosity, shown in Figure 11.3.1, was a robotic laboratory that NASA landed on Mars in 2012. Curiosity had a mass spectrometer to detect key elements required for life, in particular, carbon, oxygen, nitrogen, phosphorus and sulfur.

Mass spectrometry is often combined with other instrumental techniques for the analysis of complex mixtures, however you will apply it to pure samples.

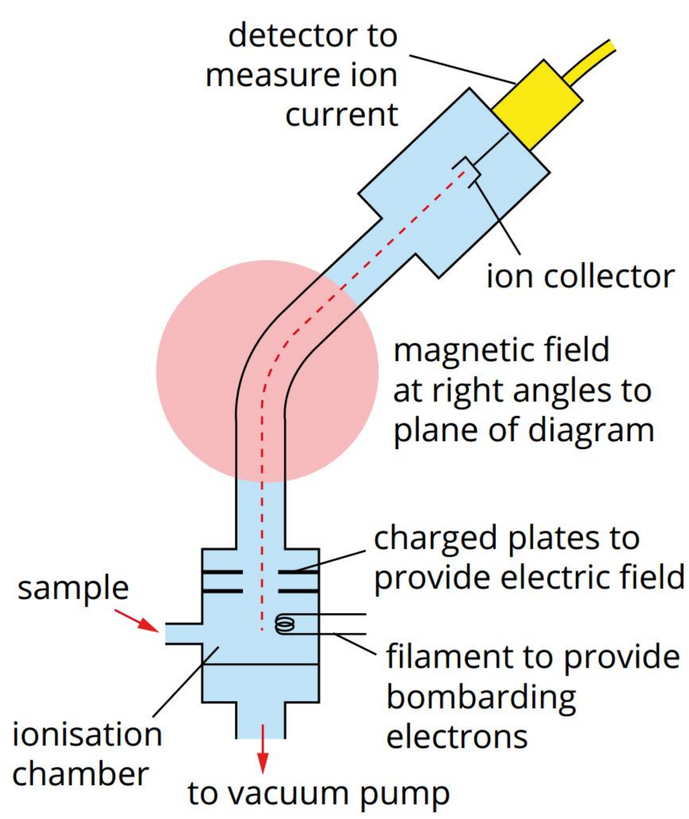


FIGURE 11.3.2 A representation of the components of a mass spectrometer

PRINCIPLES OF MASS SPECTROMETRY

A schematic diagram of a mass spectrometer is shown in Figure 11.3.2.

In a mass spectrometer:

- a sample is injected into an ionisation chamber, where it is bombarded with electrons. This causes particles to have an electron 'knocked off', which gives them a positive charge. This also causes some of the particles to fragment
- the ions are separated in a magnetic field on the basis of their mass (m)-to-charge (z) ratio (m/z) value
- the number of ions with different m/z values is measured by a detector, and the data are recorded as a **mass spectrum**.

Features of a mass spectrum

A mass spectrum of a sample of pentane is shown in Figure 11.3.3. It is a plot of the abundance, measured as **relative intensity**, of ions of different m/z. The tallest peak is given a value of 100%, then the height of the other peaks is expressed as a percentage of this value. This spectrum shows the positive ions formed when a sample of pentane was injected into the mass spectrometer. The mass in m/z is the mass number, not relative atomic mass. Therefore, in Figure 11.3.3, the masses in m/z are based on 12-carbon and 1-hydrogen.

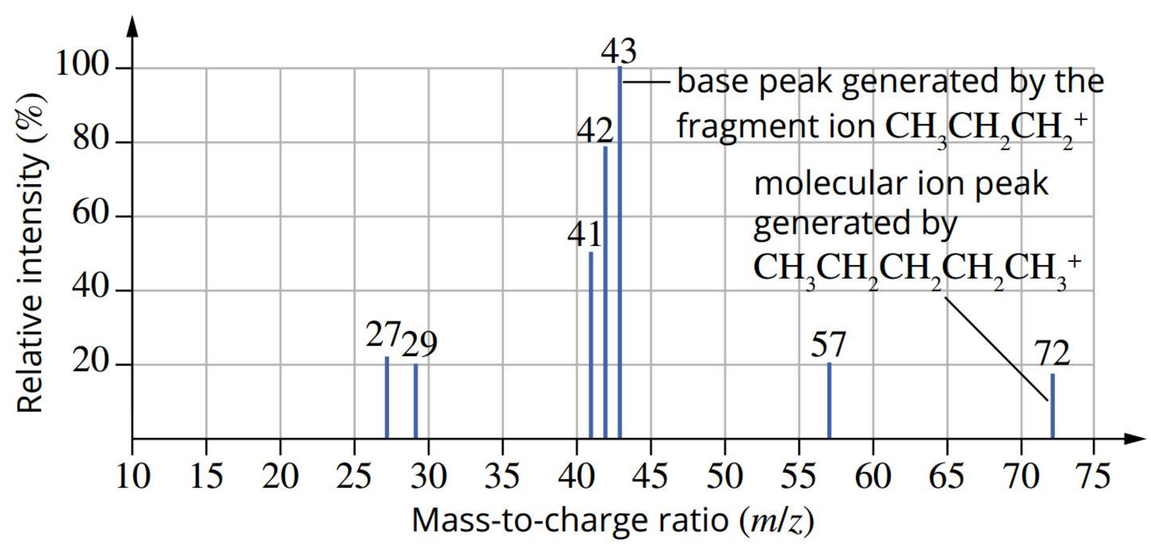


FIGURE 11.3.3 A mass spectrum of pentane ($CH_3CH_2CH_2CH_2CH_3$)

The peak at $m/z = 72$ in pentane's mass spectrum is the **molecular ion peak**. A **molecular ion**, sometimes called a parent molecular ion, is formed when the entire molecule loses an electron and becomes positively charged. When ions have a 1+ charge, meaning $z = 1$, then the m/z ratio is the same as the molecular mass of the ion. This is the case for most peaks in a mass spectrum. Peaks that may be due to the presence of particles with higher charges (and therefore have masses that do not equal the m/z ratio) are rare and are beyond the scope of this course. Note that the molecular ion peak may be very small in a mass spectrum.

The other peaks in the spectrum, which have smaller m/z values than the molecular ion, represent fragment ions. These are smaller parts of the molecule and are formed when the high-energy electrons in the ionisation chamber cause bonds to break, which then causes the molecule to break into pieces.

The most intense peak, $m/z = 43$, is called the **base peak** and is produced by the most abundant and stable fragment ion. The base peak is assigned a relative intensity of 100%. The intensity of all the other peaks are measured relative to the base peak (Figure 11.3.3). The relative intensities of the peaks in the spectrum depend on the:

- ease with which fragments can be formed
- stability of the fragment ions formed.

Fragmentation

Inside the ionisation chamber, high-energy electrons ionise the sample by knocking off electrons, producing a positive molecular ion. Because covalent bonds are formed from the sharing of electrons, the removal of electrons can cause the bonds to weaken and break.

The **fragmentation** of the molecule into smaller pieces is represented in the mass spectrum by peaks with an m/z smaller than the molecular ion. Fragments can be produced by the breaking of almost any bond in the molecular ion. They may represent single atoms, small groups of atoms or large sections of the parent molecule.

The m/z values and formulas of some common fragment ions in mass spectra of organic molecules are listed in Table 11.3.1.

The mass spectrometer only detects positively charged ions. Therefore, all detected fragments must be written with a positive charge, e.g. CH_3^+.

INTERPRETATION OF MASS SPECTRA

The information that is provided by mass spectrometry can be illustrated by examining the mass spectrum of ethanoic acid.

Ethanoic acid (CH_3COOH) can be ionised in a mass spectrometer by removing an electron in the following process:

$$CH_3COOH + e^- \rightarrow CH_3COOH^+ + 2e^-$$

The mass spectrometer gives very accurate information about the mass of positive ions formed in the instrument. The highest mass is due to the ion of the intact molecule.

TABLE 11.3.1 Common positive fragment ions

m/z	Formula
15	CH_3^+
17	OH^+
29	$CH_3CH_2^+$, CHO^+
31	CH_3O^+
35, 37	$^{35}Cl^+$, $^{37}Cl^+$
42	CH_2CO^+
43	$CH_3CH_2CH_2^+$, CH_3CO^+
45	$COOH^+$
60	CH_3COOH^+
79, 81	$^{79}Br^+$, $^{81}Br^+$

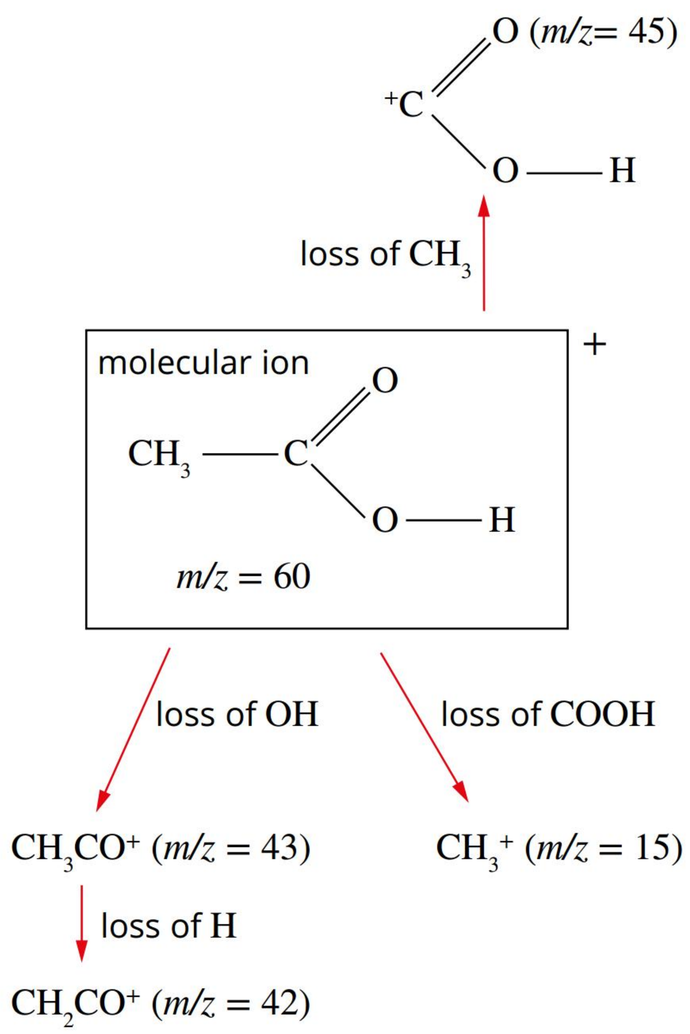


FIGURE 11.3.4 Formation of fragment ions from ethanoic acid

The molecular ion, CH_3COOH^+, is unstable and can break into a number of fragment ions, as shown in Figure 11.3.4.

The equations showing a formation of the fragments from the molecular ion:

$$CH_3COOH^+ \rightarrow CH_3CO^+ + OH$$
$$CH_3COOH^+ \rightarrow CH_3^+ + COOH$$
$$CH_3COOH^+ \rightarrow COOH^+ + CH_3$$

Note that the fragments OH, COOH and CH_3 have no charge and are therefore not detected.

The molecular and fragment ions generate peaks in the mass spectrum of ethanoic acid, as shown in Figure 11.3.5.

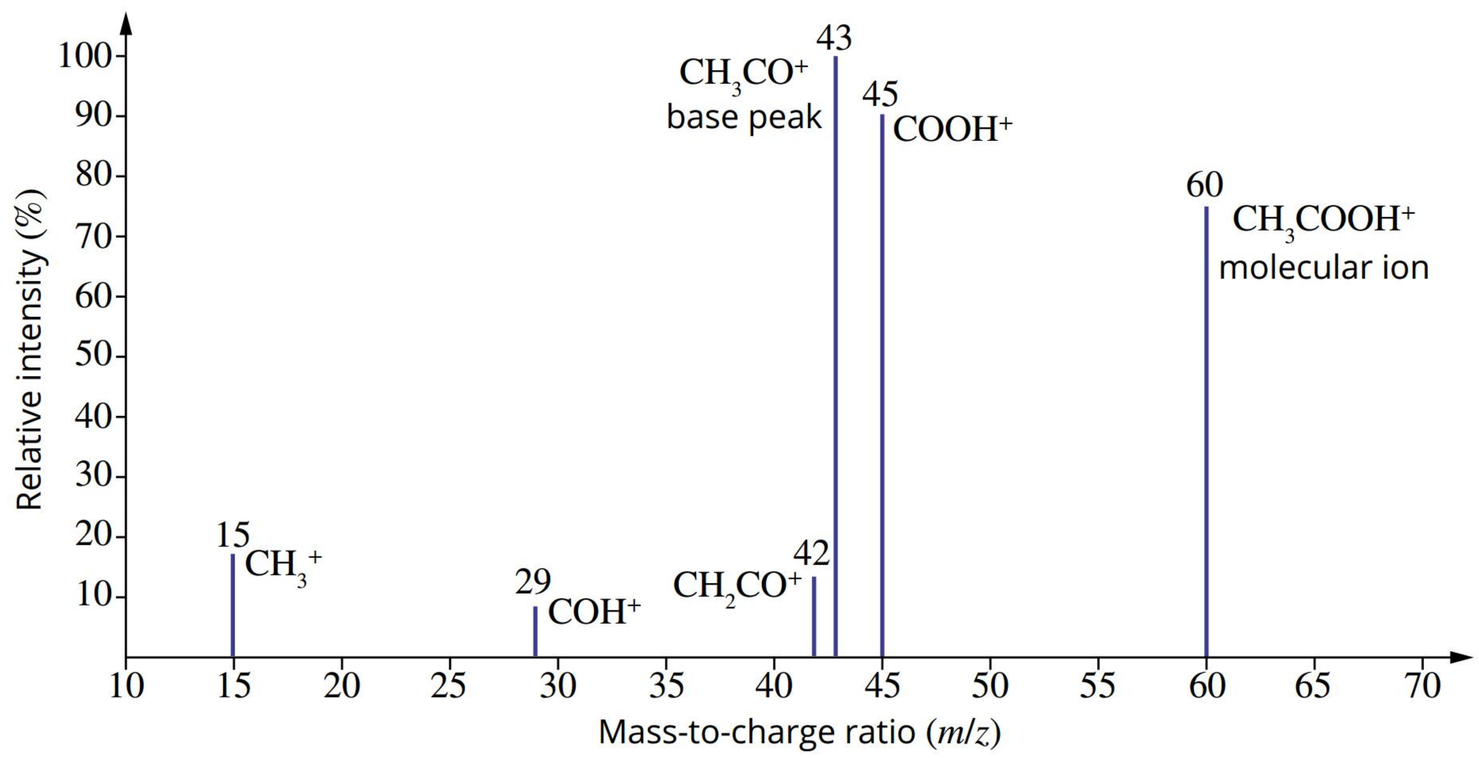


FIGURE 11.3.5 Mass spectrum of ethanoic acid

The mass in *m/z* value is the mass number, not the relative atomic mass.

The mass spectrum of ethanoic acid indicates that the molecular ion has a mass of 60. The mass of the molecular ion is the same as the relative molecular mass of the ethanoic acid molecule. The fragment ions provide information about the structure of the ethanoic acid molecule, as shown in Table 11.3.2.

TABLE 11.3.2 Identity of peaks in ethanoic acid mass spectrum

m/z	Ion identity	
60	CH_3COOH^+	molecular ion caused by the loss of an electron
45	$COOH^+$	loss of CH_3 from the molecular ion
43	CH_3CO^+	loss of OH from the molecular ion
42	CH_2CO^+	loss of H from CH_3CO^+
29	COH^+	loss of an O atom from $COOH^+$
15	CH_3^+	loss of COOH from the molecular ion

Worked example 11.3.1

DETERMINING THE IDENTITY OF A COMPOUND FROM ITS MOLECULAR ION

The mass spectrum of an unbranched alkane has a molecular ion peak of $m/z = 86$. Determine the molecular formula of the alkane and state its name.	
Thinking	**Working**
The m/z value of the molecular ion is equal to the molecular mass of the molecule.	The relative molecular mass of the alkane is 86.
Identify the general formula for the molecule.	The general formula for an alkane is C_nH_{2n+2}.
Use the general formula to construct an equation linking the molecular mass to the atomic masses of the constituent atoms.	mass of $^{12}C = 12$ mass of $^{1}H = 1$ $(12 \times n) + (1 \times (2n + 2)) = 86$
Solve the equation for n.	$12n + 2n + 2 = 86$ $14n + 2 = 86$ $14n = 84$ $n = 6$
Use the value of n to find the molecular formula and the name.	C_6H_{14}, which is hexane

➤ Try yourself 11.3.1

DETERMINING THE IDENTITY OF A COMPOUND FROM ITS MOLECULAR ION

The mass spectrum of an unbranched alkane has a molecular ion peak of $m/z = 58$. Determine the molecular formula of the alkane and state its name.

Differentiating between molecules with the same molecular mass

Methyl propanoate and ethyl ethanoate are both esters and have the same molecular formula, $C_4H_8O_2$. The mass of the molecular ion for both molecules is the same; therefore, fragment ions have to be used to provide more information for identification.

Methyl propanoate and ethyl ethanoate both have a molecular ion at $m/z = 88$. The possible fragment ions differ slightly for each molecule, as seen in the mass spectra in Figure 11.3.6.

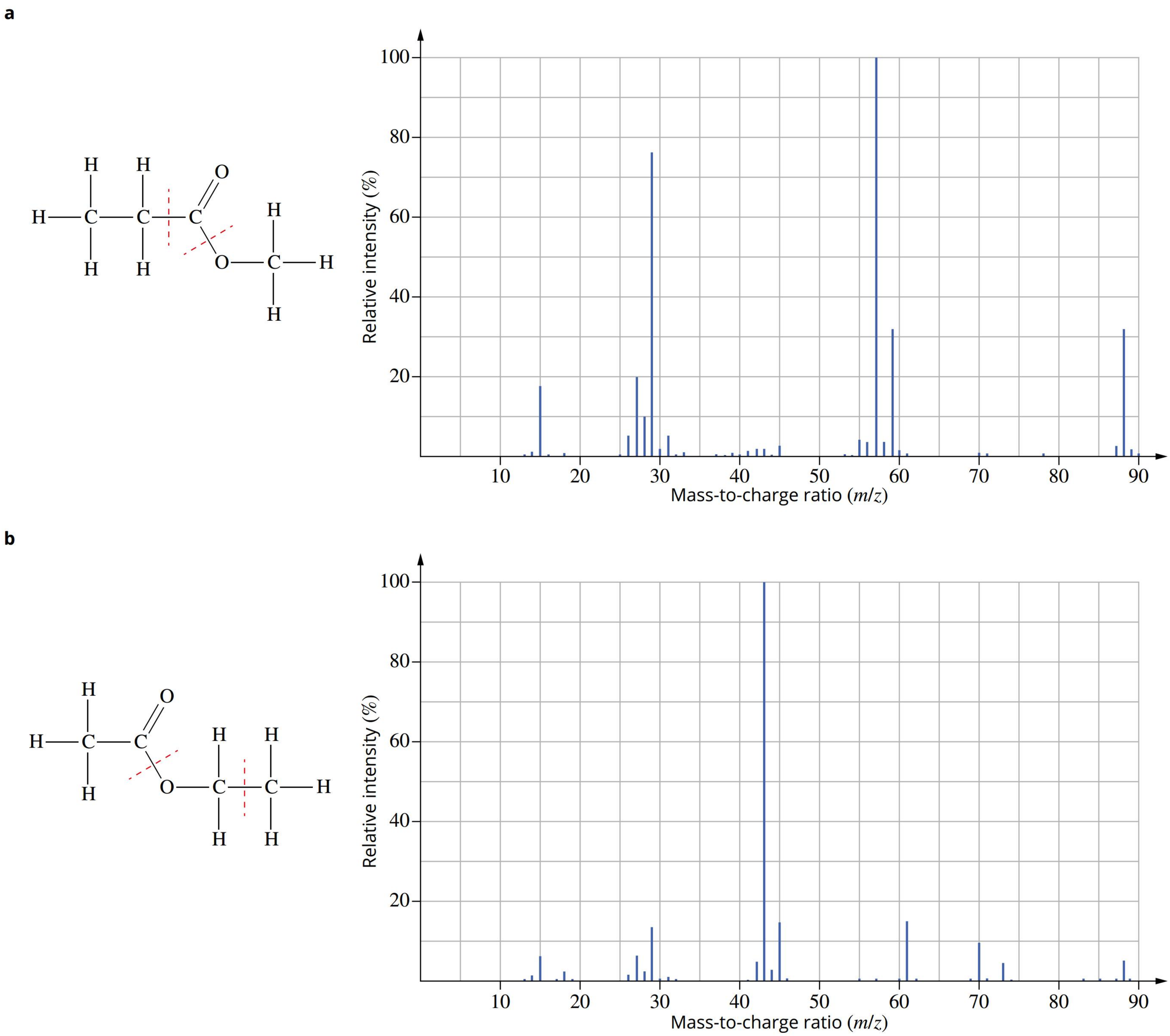


FIGURE 11.3.6 The structural formula and mass spectrum of (a) methyl propanoate and (b) ethyl ethanoate

The mass spectrum of methyl propanoate has the following distinguishing fragment ions.

- The peak at $m/z = 57$ is due to fragment ion $CH_3CH_2CO^+$.
- The peak at $m/z = 29$ is due to fragment ion $CH_3CH_2^+$.

The mass spectrum of ethyl ethanoate has the following distinguishing fragment ions.

- The peak at $m/z = 43$ is due to fragment ion CH_3CO^+.
- The peak at $m/z = 45$ is due to fragment ion $OCH_2CH_3^+$.
- The peak at $m/z = 73$ is due to fragment ion $CH_3COOCH_2^+$.

Isotope effects

Most elements exist as mixtures of isotopes, as shown in Table 11.3.3. The presence of stable isotopes in molecules leads to the appearance of additional peaks in a mass spectrum.

TABLE 11.3.3 Stable isotopes of some atoms and their percentage abundance

Element	Isotope	Isotopic mass	Percentage abundance	Isotope	Isotopic mass	Percentage abundance
hydrogen	^{1}H	1.0	99.98	^{2}H	2.0	0.02
carbon	^{12}C	12.0	98.9	^{13}C	13.0	1.1
oxygen	^{16}O	16.0	99.8	^{18}O	18.0	0.2
chlorine	^{35}Cl	35.0	75.8	^{37}Cl	37.0	24.2
bromine	^{79}Br	79.0	50.7	^{81}Br	81	49.3

The percentage abundance of ^{2}H, ^{13}C and ^{18}O in samples is very small, so ions containing them only produce very small peaks in the mass spectra. The presence of these isotopes can be ignored in most instances. However, chlorine and bromine have high proportions of each isotope, and so samples that contain them have significant peaks for each isotope in their mass spectra.

The mass spectrum of chloromethane (CH_3Cl) shows peaks for two molecular ions (Figure 11.3.7).

- The peak at $m/z = 50$ is due to the molecular ion containing ^{35}Cl.
- The peak at $m/z = 52$ is due to the other molecular ion containing ^{37}Cl.

The relative heights of these peaks reflect the relative abundance of the two isotopes.

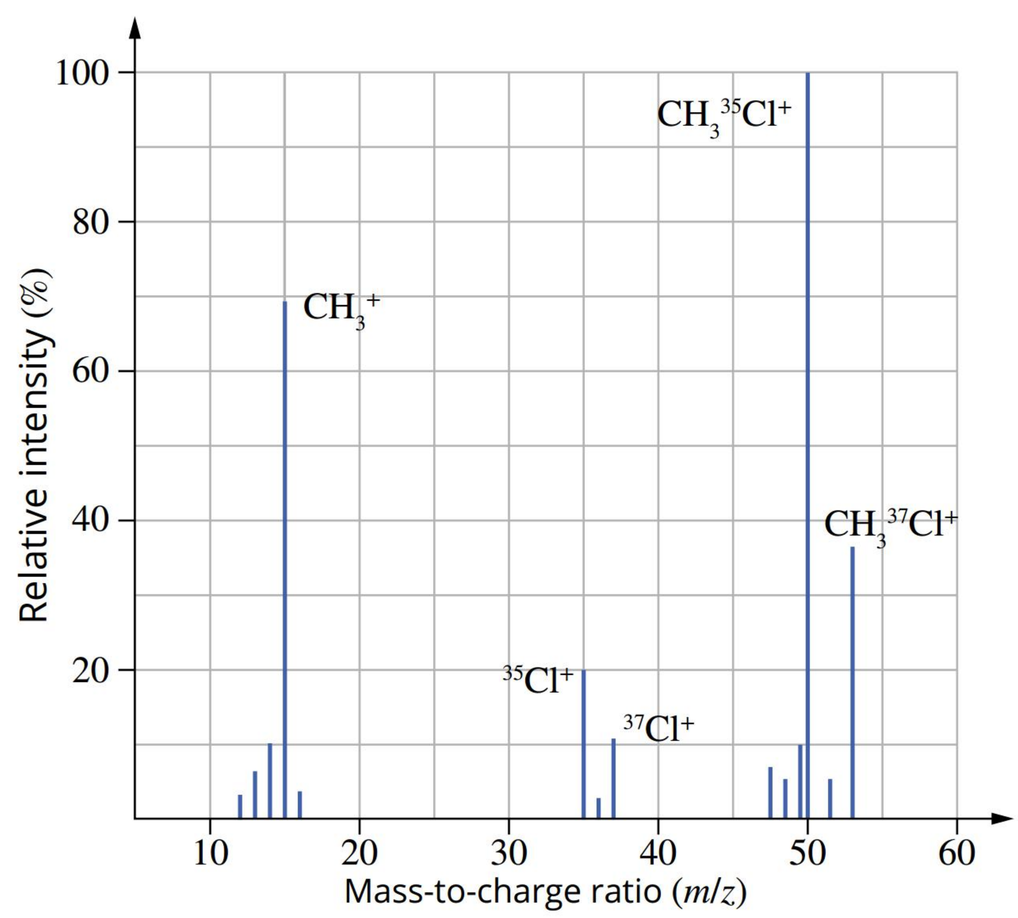


FIGURE 11.3.7 The mass spectrum of chloromethane (CH_3Cl). Note the two molecular ion peaks due to the isotopes of chlorine

As the number of atoms that have significant proportions of isotopes increases, the mass spectrum can become more complex. The mass spectrum of dichloromethane (CH_2Cl_2) shows three molecular ion peaks (Figure 11.3.8).

- The peak at $m/z = 84$ is due to the molecular ion containing two ^{35}Cl atoms.
- The peak at $m/z = 86$ is due to the molecular ion containing one ^{35}Cl atom and one ^{37}Cl atom.
- The peak at $m/z = 88$ is due to the molecular ion containing two ^{37}Cl atoms.

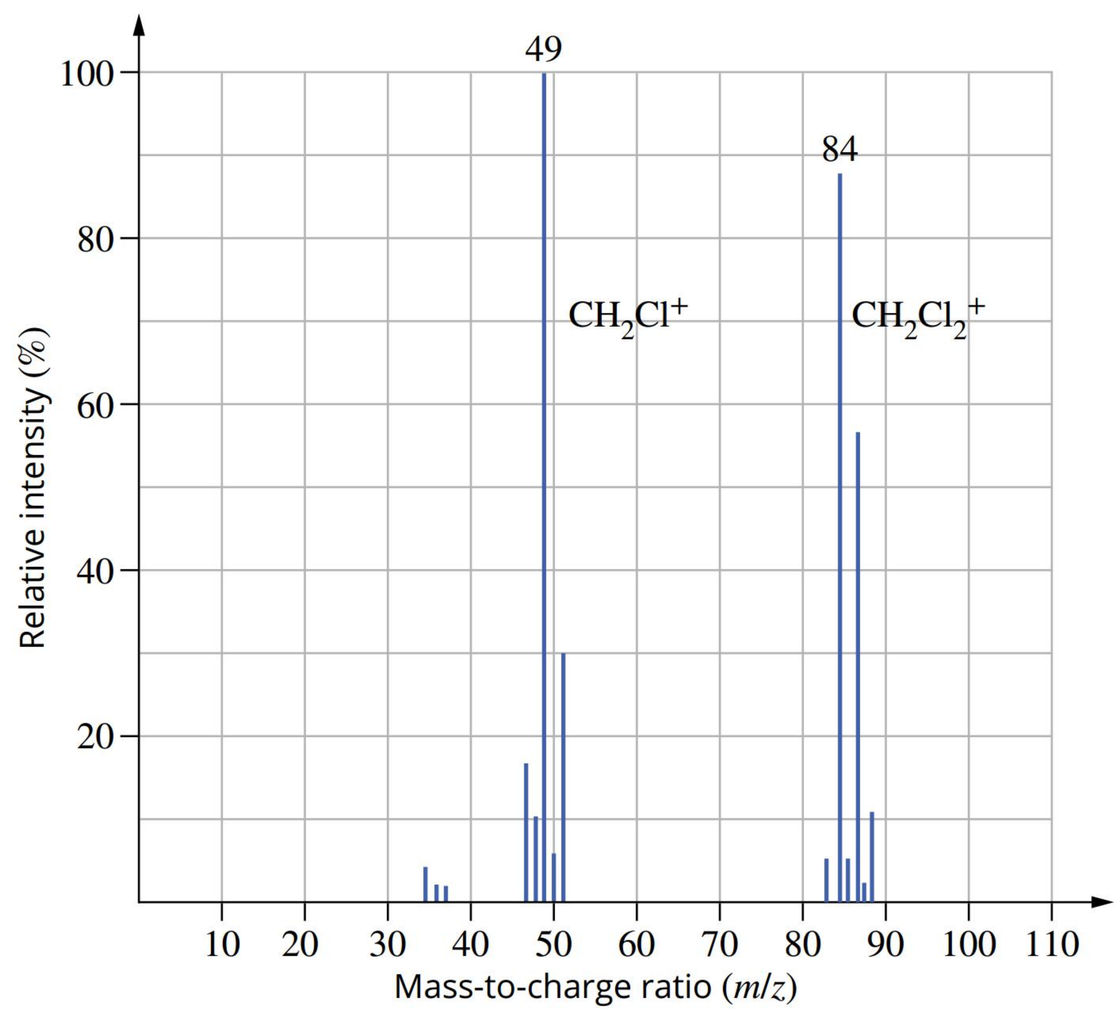


FIGURE 11.3.8 The mass spectrum of dichloromethane (CH_2Cl_2). Note the three molecular ion peaks at $m/z = 84$, 86 and 88 due to the isotopes of chlorine

Using mass spectroscopy for determining the empirical formula

In Unit 1, you learnt about calculating the empirical formula and the molecular formula of compounds using the percentage composition of elements. In this section, we will use percentage composition data and mass spectroscopy data to determine the empirical and molecular formulas of unknown compounds.

You have learnt that the percentage composition of a compound is the proportion by mass of the different elements in that compound.

Percentage composition is calculated by the following formula:

$$\frac{\text{mass of element in 1 mol of the compound}}{\text{mass of 1 mol of the compound}} \times 100$$

The empirical formula is the simplest whole-number ratio of elements in a compound.

The empirical formula can be calculated from the percentage composition by dividing each mass by the relative atomic mass to determine the number of moles for each element in the compound. The number of moles for each element is converted to a whole number.

In order to determine the formula of an unknown compound, the percentage composition can be determined experimentally. Once the mass of each element in the compound is known, it is possible to determine an empirical formula. The molecular formula is calculated from the empirical formula by using the molecular mass of the compound which is determined using mass spectrometry. In these calculations, the vital information regarding the mass of the intact molecule is provided by identifying the molecular ion peak on the mass spectrum.

Worked example 11.3.2

DETERMINING THE EMPIRICAL FORMULA OF A COMPOUND FROM ITS PERCENTAGE COMPOSITION.

Chemical analysis of an unknown organic compound shows that its percentage composition is 16.37% hydrogen and 83.63% carbon by mass. Determine the empirical formula of the compound.

Thinking	Working
Calculate the number of moles for each element using the relative abundance as mass in grams.	$n(\text{H}) = \frac{16.37}{1.01}$ $n(\text{C}) = \frac{83.63}{12.01}$ $n(\text{H}) = 16.21\,\text{mol}$ $n(\text{C}) = 6.96\,\text{mol}$
Simplify the ratio to obtain whole numbers.	$\frac{16.21}{6.96}$ $\frac{6.96}{6.96}$ $= 2.33 \times 3$ $= 1.00 \times 3$ $= 6.99$ $= 3$ $= 7$ $= 3$
Write the empirical formula.	C_3H_7

➤ Try yourself 11.3.2

DETERMINING THE EMPIRICAL FORMULA OF A COMPOUND FROM ITS PERCENTAGE COMPOSITION

Chemical analysis of an unknown compound shows that its percentage composition is 17.75% hydrogen and 82.24% nitrogen by mass. Determine the empirical formula of the compound.

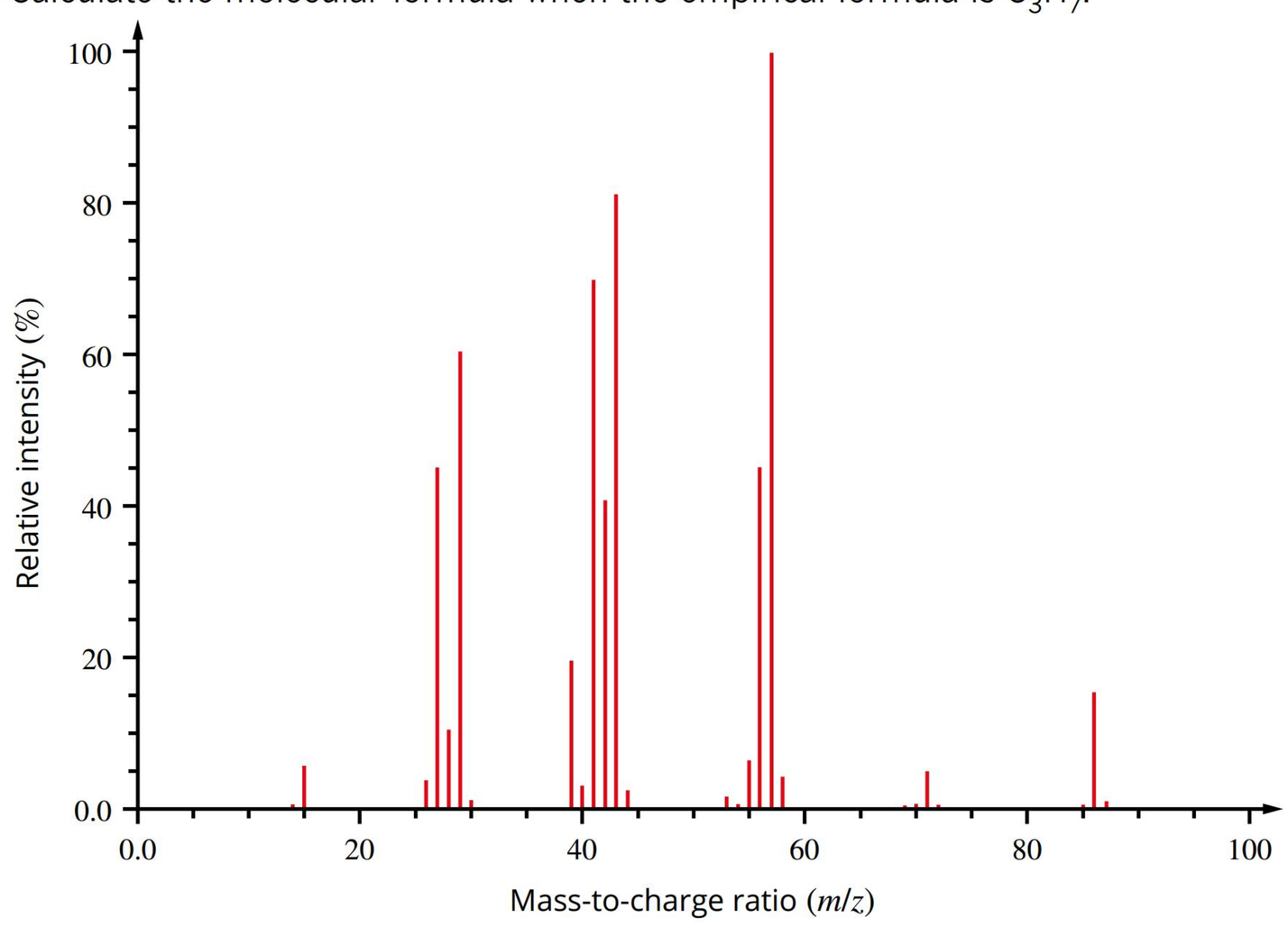
The molecular formula is determined by using the molecular ion peak from the molecular mass spectrum and the empirical formula of your unknown compound. Note that the molecular mass spectrum is described earlier in this module, where it displays the fragmentation peaks.

Worked example 11.3.3

DETERMINING THE MOLECULAR FORMULA OF A COMPOUND FROM ITS MOLECULAR MASS SPECTRUM AND EMPIRICAL FORMULA

The mass spectrum below shows a molecular mass spectrum of an unknown compound.

Calculate the molecular formula when the empirical formula is C_3H_7.

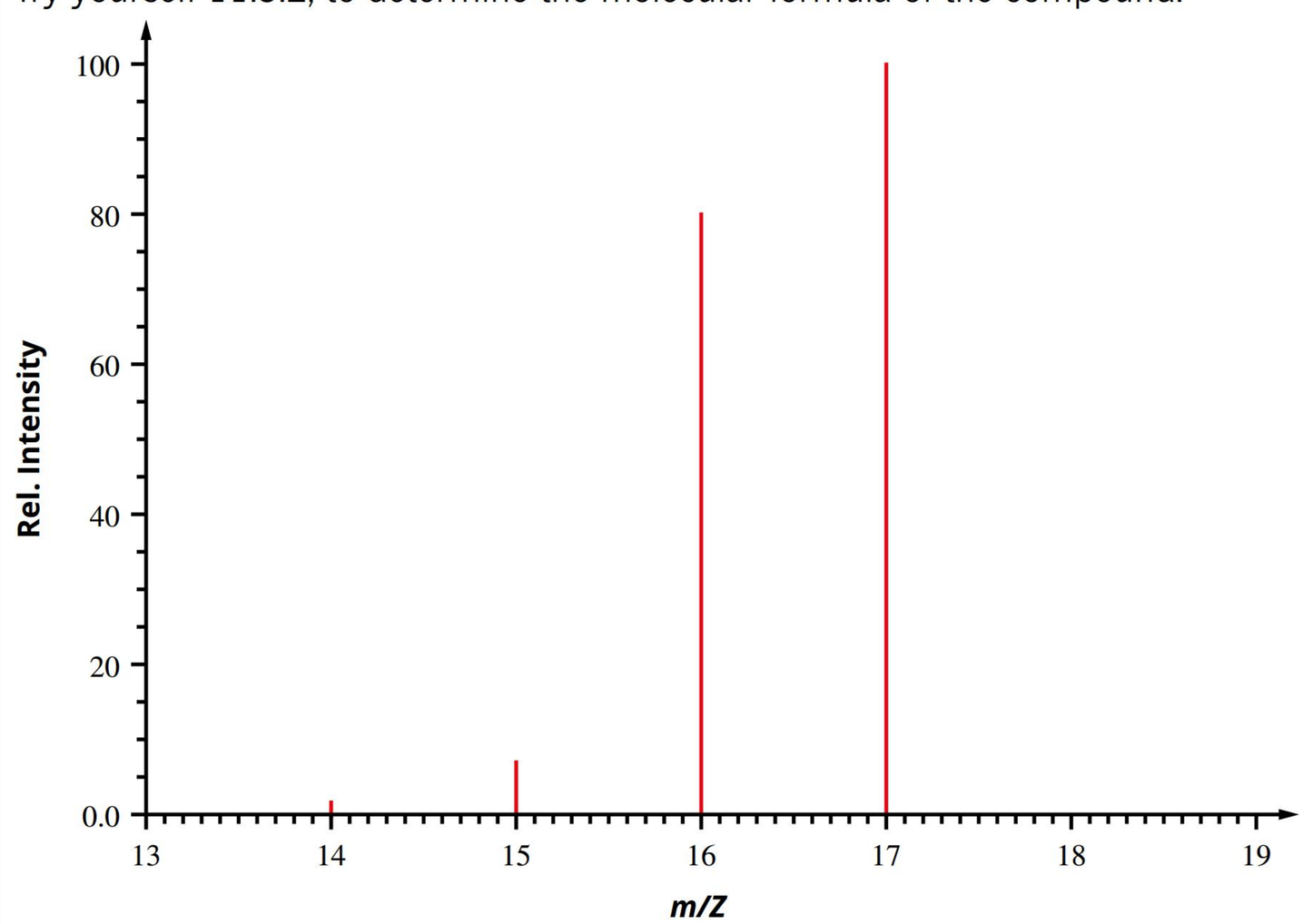


Thinking	Working
Find the molecular ion peak on the mass spectrum and determine the molecular mass.	$m/z = 86$ Molecular mass = 86 g mol^{-1}
Calculate the molar mass of the empirical formula using mass numbers.	$m(C_3H_7) = (3 \times 12) + (7 \times 1)$ $m(C_3H_7) = 43\,g\,mol^{-1}$
Determine the number of empirical formula units in the molecular formula by dividing the molar mass of the compound by the molar mass of the empirical formula.	Number of empirical units $= \frac{86}{43}$ $= 2$
Multiply the subscripts of the empirical formula by the number of empirical formula units to get the molecular formula.	Molecular formula $= 2 \times C_3H_7$ $= C_6H_{14}$

➤ Try yourself 11.3.3

DETERMINING THE MOLECULAR FORMULA OF A COMPOUND FROM ITS MOLECULAR MASS SPECTRUM AND EMPIRICAL FORMULA

Use the mass spectrum of an unknown compound below, and your answer in Try yourself 11.3.2, to determine the molecular formula of the compound.



11.3 Review

SUMMARY

- A mass spectrometer measures the mass-to-charge ratio, *m/z*, of ions.
- The peak that has the highest *m/z* is usually caused by the entire molecule becoming ionised and is called the molecular ion peak.
- The molecular ion can break into pieces called fragment ions.
- Fragmentation of a molecule in a mass spectrometer can help to determine its molecular structure.
- Each compound has a unique mass spectrum that can be used to identify its structural, molecular and empirical formulas.
- The mass spectrum of a compound containing chlorine or bromine atoms has significant additional peaks due to the isotopes of chlorine and bromine.
- Analyse data from the atomic mass spectrum to determine the percentage composition and empirical formula.

KEY QUESTIONS

Describe

1 Define the following terms.

a molecular ion

b base peak

c mass-to-charge ratio

2 Recall what additional peaks next to the main molecular ion peak in the mass spectrum indicate.

3 A student was asked to identify the fragment that may have caused the peak at *m/z* 29 in a mass spectrum of methanol. Explain why their answer, CHO, is incorrect, and provide the correct answer.

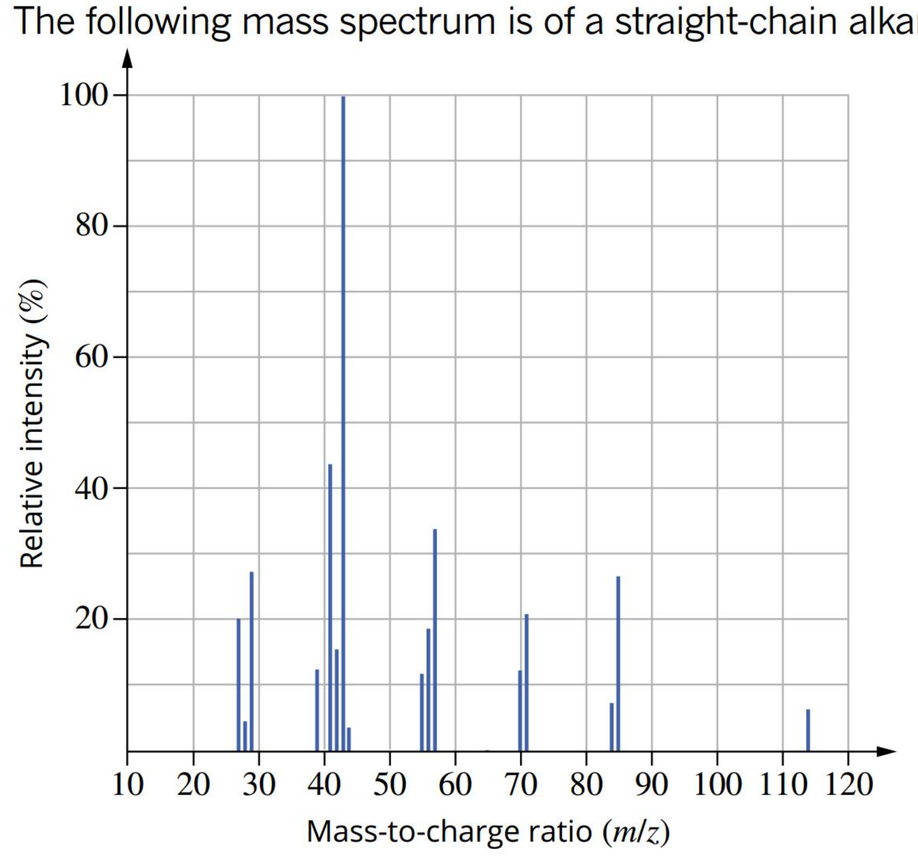
Apply

4 Calculate the empirical formula of an unknown organic compound with the following composition by mass: 6.71% hydrogen, 40.00% carbon, 53.29% oxygen.

5 List the molecular ions (including different isotopes) that would be found in the mass spectrum of 1,1-dibromoethane.

Analyse

6 The following mass spectrum is of a straight-chain alkane.

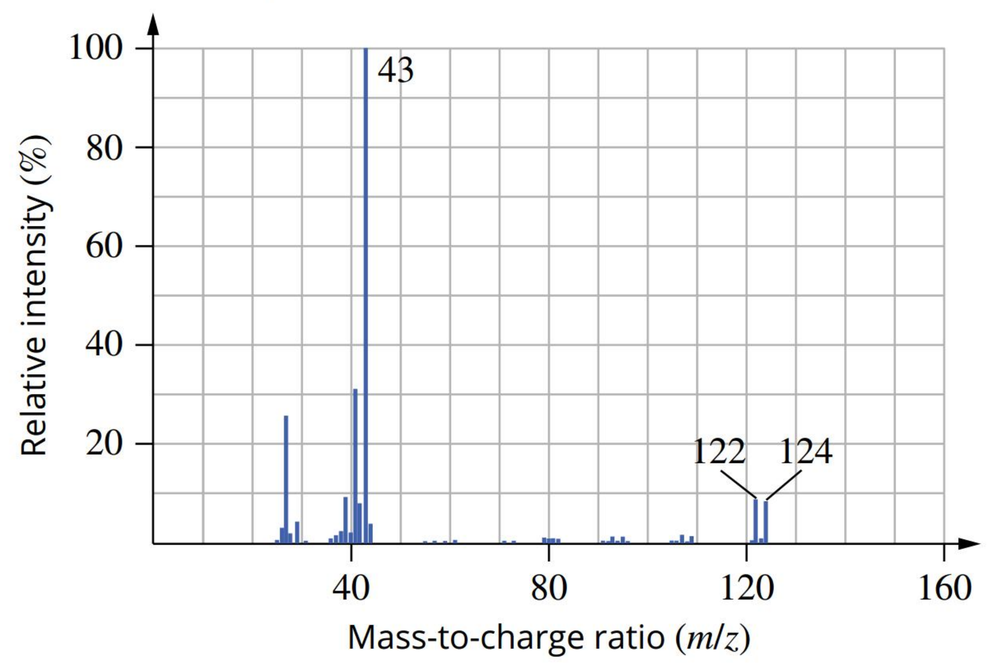


a Determine the *m/z* value of the base peak.

b State the formula for the fragment ion with an *m/z* value of 85.

c Identify the name of the alkane represented.

7 The mass spectrum of a bromoalkane is shown below.



a Determine the molecular formula of the bromoalkene.

b Explain why the mass spectrum has two peaks at *m/z* = 122 and *m/z* = 124.

c Explain why the relative heights of these two peaks are almost the same.

d Write a possible formula for the ion responsible for the peak at *m/z* = 43.

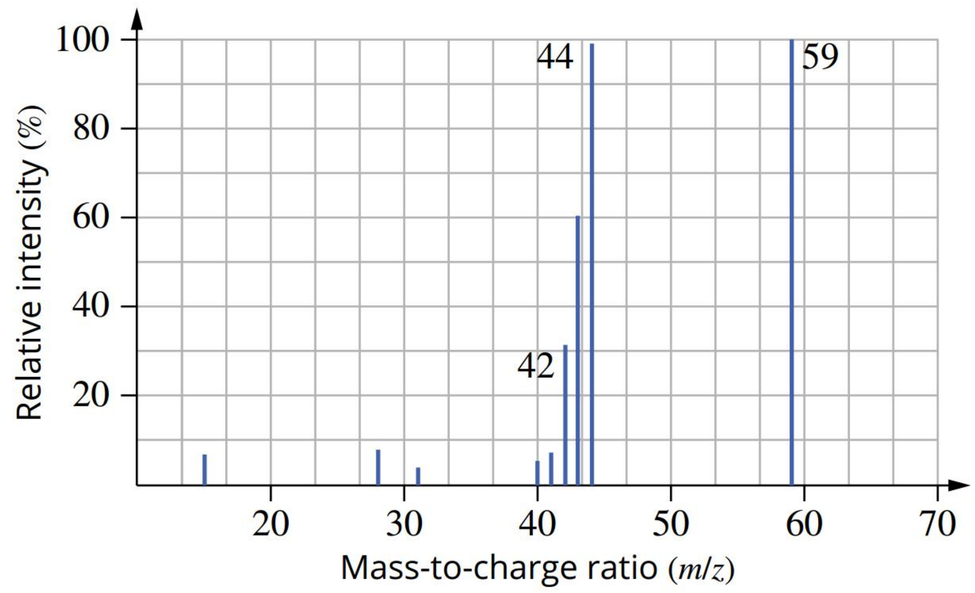
8 Determine the structural formula of the molecules using the following mass spectra.

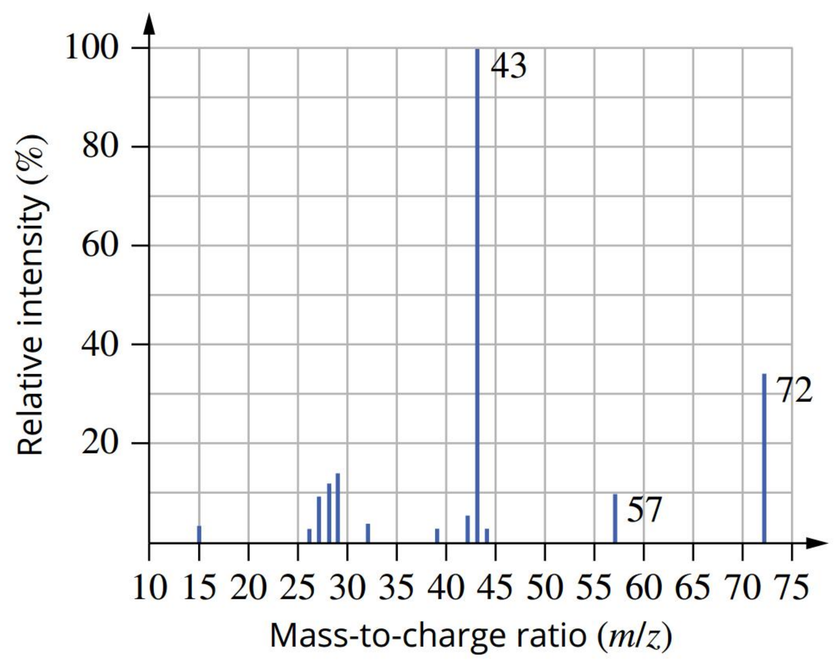
a Figure A represents an unknown amide.

b Figure B represents an unknown ketone.

Continued over page

11.3 Review *continued*



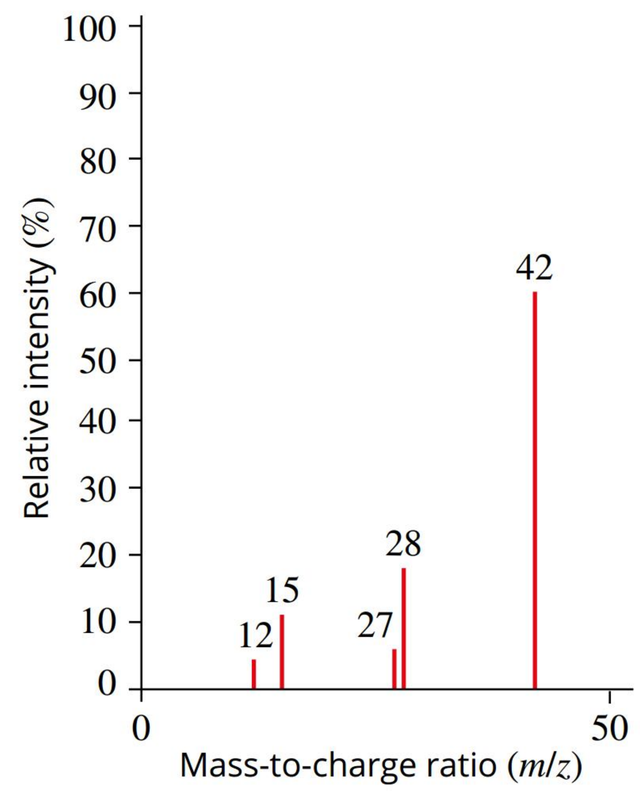


9 The mass spectrum of an unknown alkene is shown below.

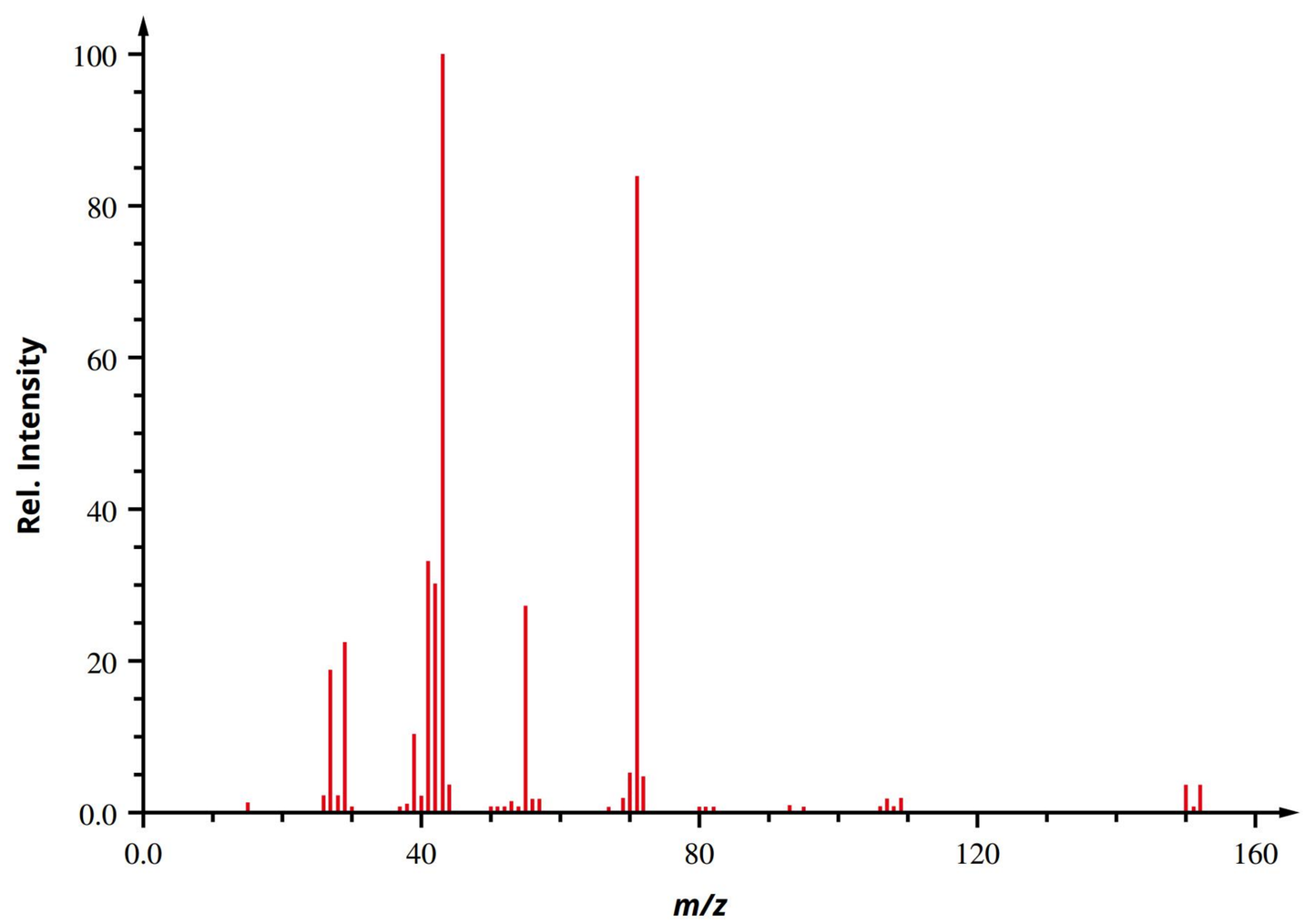
a Identify the molecular ion peak.

b State the relative molecular mass of the unknown alkene.

c Determine the molecular formula of the alkene and state its name.



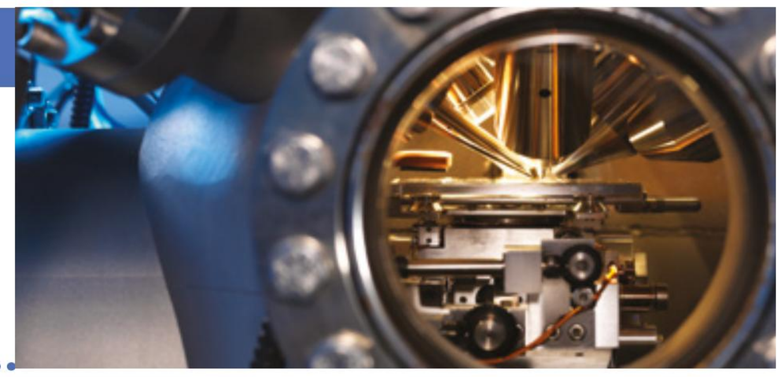
10 Identify the following bromoalkane using the mass spectrum provided below.



11.4 Infrared spectroscopy

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- explain how infrared (IR) radiation influences the vibrational energy in atoms and molecules
- use IR spectroscopy to determine bond types and functional groups in organic molecules.



All types of spectroscopy use electromagnetic radiation to give information about the materials around you. Spectroscopy utilises the effects of electromagnetic radiation on atoms and molecules to learn about their structure.

The **electromagnetic spectrum** shown in Figure 11.4.1 is divided into different regions of radiation, with different frequencies, wavelengths and energies. Ultraviolet light has short wavelengths with high frequency and energy, whereas radio waves have long wavelengths and low frequency and energy.

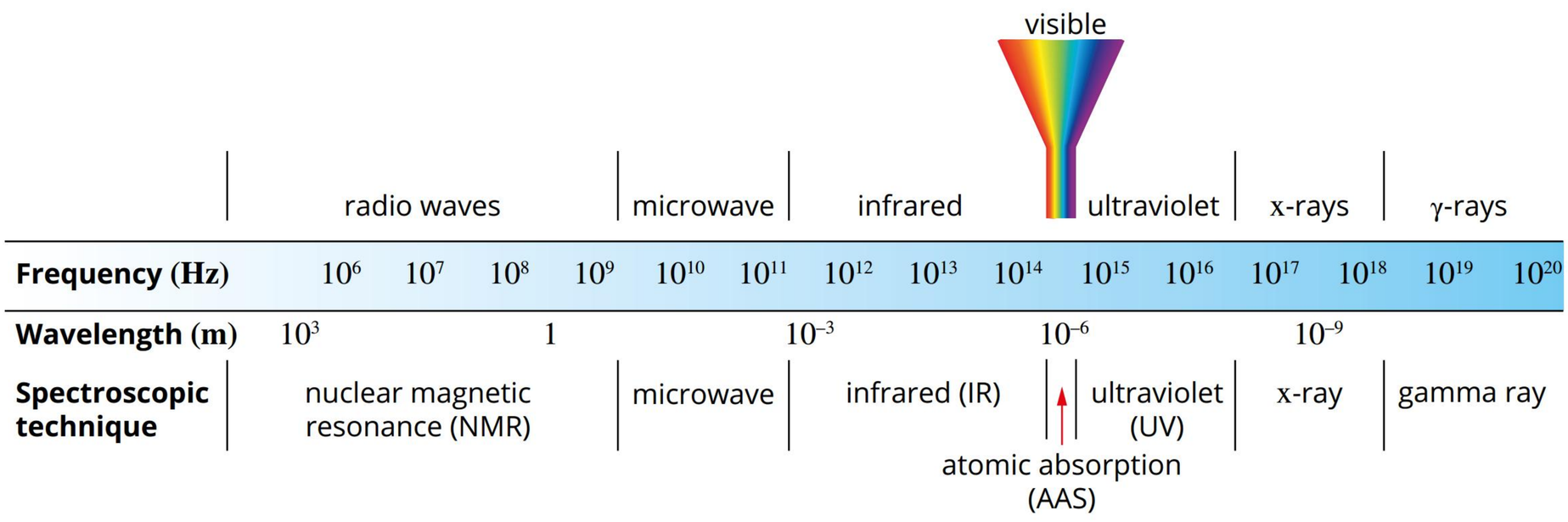


FIGURE 11.4.1 The electromagnetic spectrum showing the frequency and wavelength of different regions and their applications to spectroscopy

Atoms and molecules contain different types of energy related to the electron configuration, the covalent bonds present and the movement of the molecule itself. For example, the water molecule in Figure 11.4.2 shows four different types of energy in order of increasing energy.

Spectroscopic techniques use the facts that:

- atoms and molecules absorb and emit electromagnetic radiation of specific energies
- atoms and molecules undergo a change when they absorb electromagnetic radiation
- vibrational energy of covalent bonds is measured in the infrared regions.

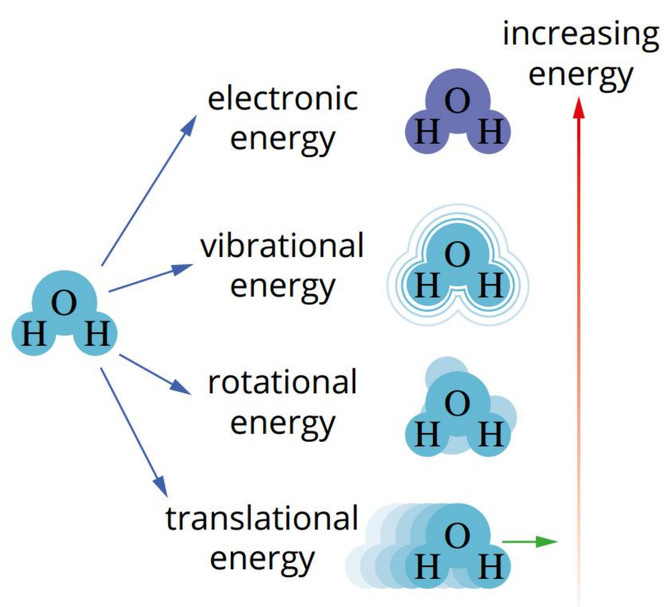


FIGURE 11.4.2 A water molecule has different types of energy

FIGURE 11.4.3 A food chemist uses an infrared spectrometer to evaluate the quality of raisins

PRINCIPLES OF INFRARED SPECTROSCOPY

Infrared (IR) spectroscopy is a powerful analytical tool that can be applied to the analysis of many organic and inorganic compounds.

IR spectroscopy can be used to analyse solids, liquids and gases. It is used as a quality-control tool in the pharmaceutical industry, agriculture, food processing (Figure 11.4.3), paint, paper and other industries. For example, it can be used in drug testing, as shown in Figure 11.4.4. Researchers combine IR spectroscopy with other techniques to study biological molecules. The technique is used to analyse blood and urine samples and is also used to determine the level of atmospheric pollutants.

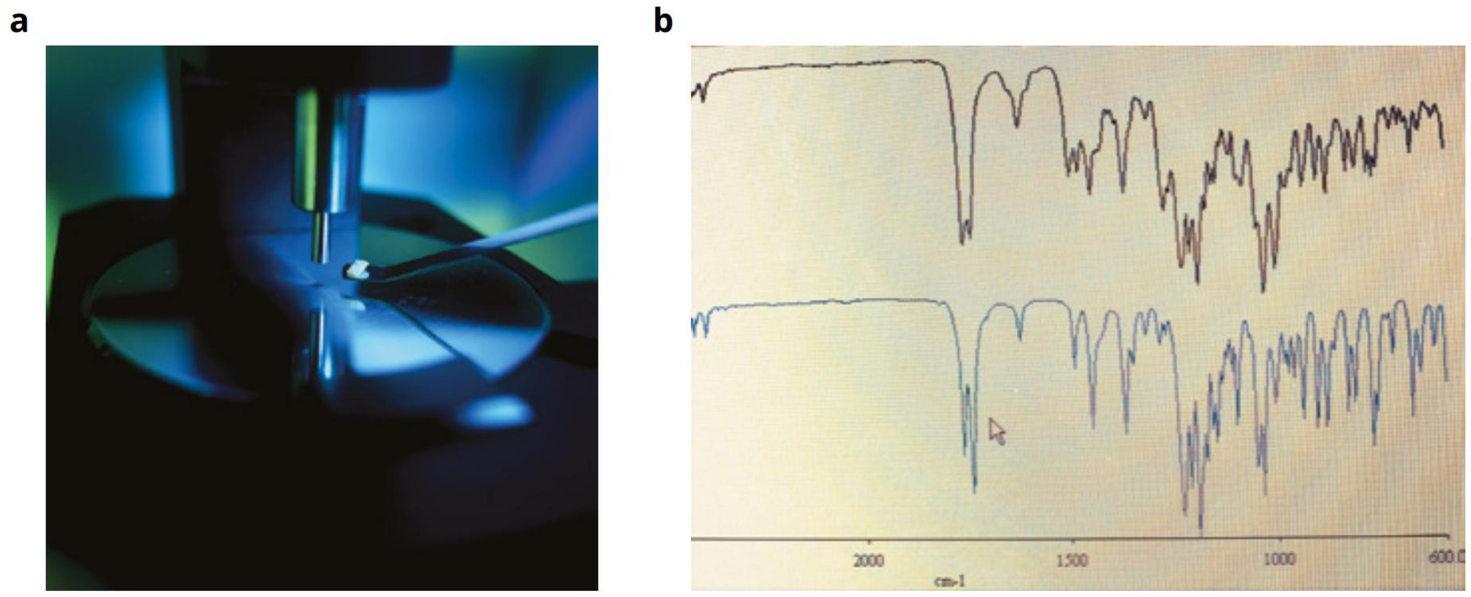


FIGURE 11.4.4 (a) Obtaining the infrared spectrum of a suspected illegal drug. (b) The spectrum of the substance (black) closely matches that of a heroin sample (blue), indicating that the substance contains the illegal drug.

IR spectroscopy is particularly useful because it can give you information about the functional groups present in an organic molecule. This information helps to clarify its structure. IR radiation has a lower energy and a longer wavelength than visible and ultraviolet light. The energy from IR radiation is enough to change the vibration of the bonds in molecules. Covalent bonds can be compared to springs that can undergo specific amounts of bending or stretching. When IR radiation is passed through a sample, specific frequencies will be absorbed and cause certain bonds to vibrate. The IR radiation is measured after it has passed through the molecule, and the patterns of **absorption** enable chemists to identify the bonds (and therefore the functional groups) present.

The frequency of absorption is dependent upon two factors:

- the strength of the bond
- the mass of the atoms involved.

We will only focus on the stretching motions covalent bonds undertake and their respective IR absorption bands.

In general, stronger bonds will absorb IR of a higher frequency and energy. For example, the C–C bond is weaker than the C=C and C≡C bonds, and therefore absorbs IR radiation of a lower frequency. The frequency of a vibration is directly proportional to the energy of the vibration. The absorption band seen on the IR spectrum for a C–C bond will have a lower **wavenumber** (cm^{-1}), or waves per unit distance (Table 11.4.1), than that of a C=C or C≡C bond.

In infrared spectroscopy, the frequency is expressed as the wavenumber, or waves per unit distance, and has the unit cm^{-1}.

TABLE 11.4.1 Bond energy, representing the strength of the bond, compared to the frequency of infrared light absorbed

Bond	Bond energy ($kJ\,mol^{-1}$)	Infrared absorption frequency (cm^{-1})	Increasing energy of vibration
C≡C	839	2100–2260	↑
C=C	614	1620–1680	
C–C	346	880	

The mass of the atoms attached to a bond also affects the frequency of the IR radiation that will be absorbed. Atoms with higher masses absorb lower-frequency radiation. Table 11.4.2 compares the energy absorbed when atoms of different masses are bonded to carbon with a single bond.

TABLE 11.4.2 Atomic mass affects the frequency of infrared light absorbed

Bond	Typical absorption frequency (cm^{-1})	Increasing energy of vibration
C–H	2720–3100	↑
C–O	1050–1410	
C–Cl	600–800	
C–Br	500–600	

Instrumentation

Figure 11.4.5 shows the main components of a simple infrared spectrophotometer. These include:

- a source of infrared radiation (electrically heated filament)
- a sample and reference cell
- a wavelength selector (monochromator)
- an infrared detector.

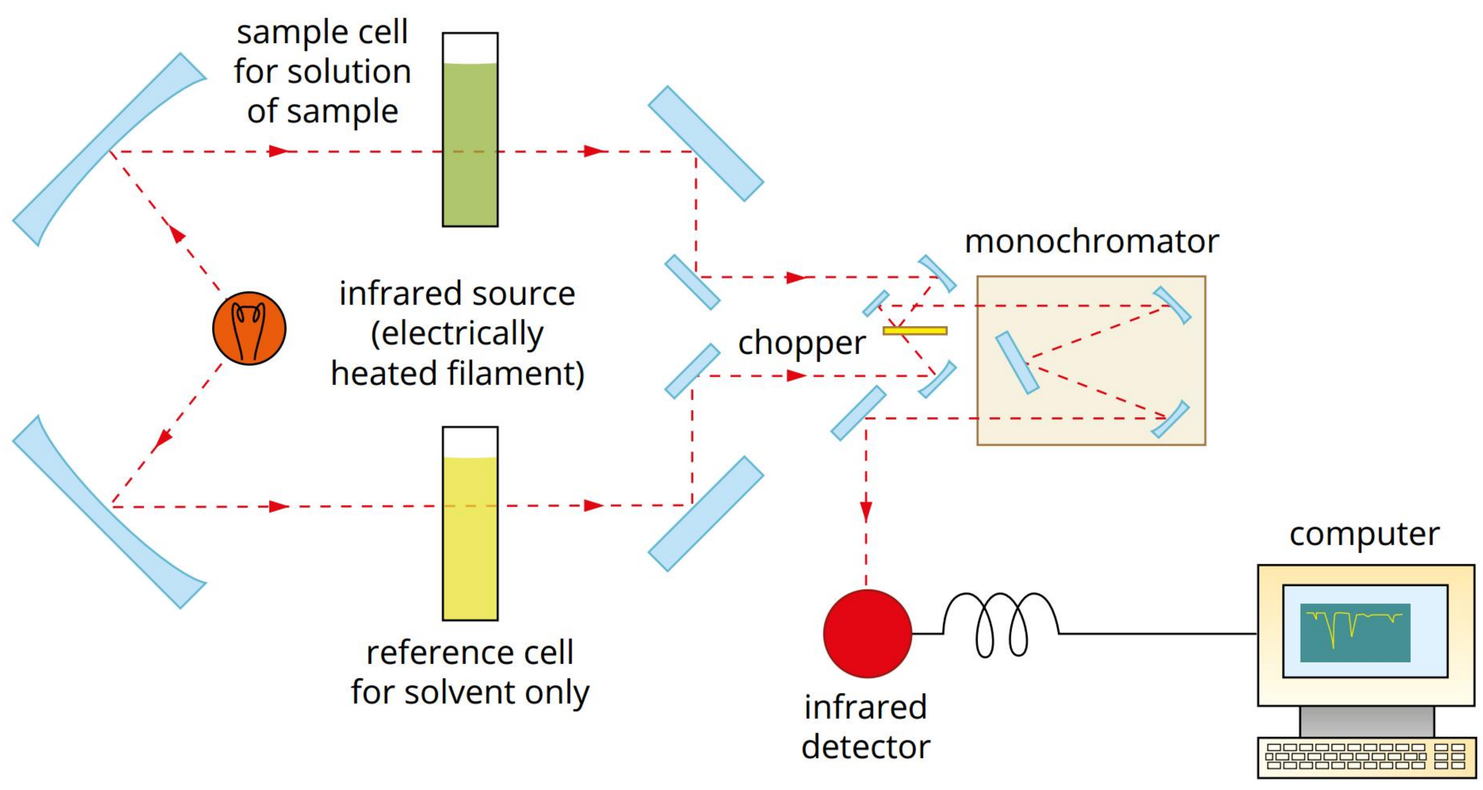


FIGURE 11.4.5 Essential features of a simple IR spectrophotometer

The IR radiation from the source is split into two beams and passed separately through the sample cell and a reference cell. The material used to contain the sample and reference is NaCl, KBr or a similar substance. Plastic or glass cannot be used as these materials absorb IR radiation. The reference cell is used to discount the effect of the material of the sample cell, the solvent and any interference from water or carbon dioxide in the atmosphere. The two beams pass through a wavelength selector (monochromator) and an infrared detector. The difference in **transmittance**, or transmitted radiation, between the sample and reference cell is due to the absorption of certain frequencies by the molecules of the sample.

INTERPRETATION OF INFRARED SPECTRA

The following section will show you how to interpret an infrared spectrum. You will learn about the key features and how to identify the functional groups present in a molecule based on the **absorption bands**, which are present or absent in an infrared spectrum.

Features of an infrared spectrum

The frequency of the electromagnetic radiation in IR spectroscopy is usually expressed in wavenumbers (cm^{-1}). The wavenumber is the number of waves per centimetre and is inversely proportional to wavelength. A bond that vibrates at a higher frequency absorbs IR radiation with a higher wavenumber and greater energy than a bond that vibrates at a lower frequency.

The horizontal axis of an IR spectrum shows the wavenumber, and the highest wavenumber is usually shown on the left. This axis often has two scales to ensure all features are visible. In the IR spectrum of 2-methylpropan-2-ol, shown in Figure 11.4.6, you can see that the scale starts with intervals of 1000 cm^{-1} and then changes to intervals of 500 cm^{-1} in the region below 2000 cm^{-1}.

The vertical axis of an IR spectrum shows the percentage transmittance on a scale of 0–100. The 'baseline' of the spectrum is where all of the light, 100%, is passed (transmitted) through the sample. Where the molecule absorbs IR radiation, the spectrum dips down to a lower transmittance. These **absorption bands** appear as inverted peaks in the spectrum.

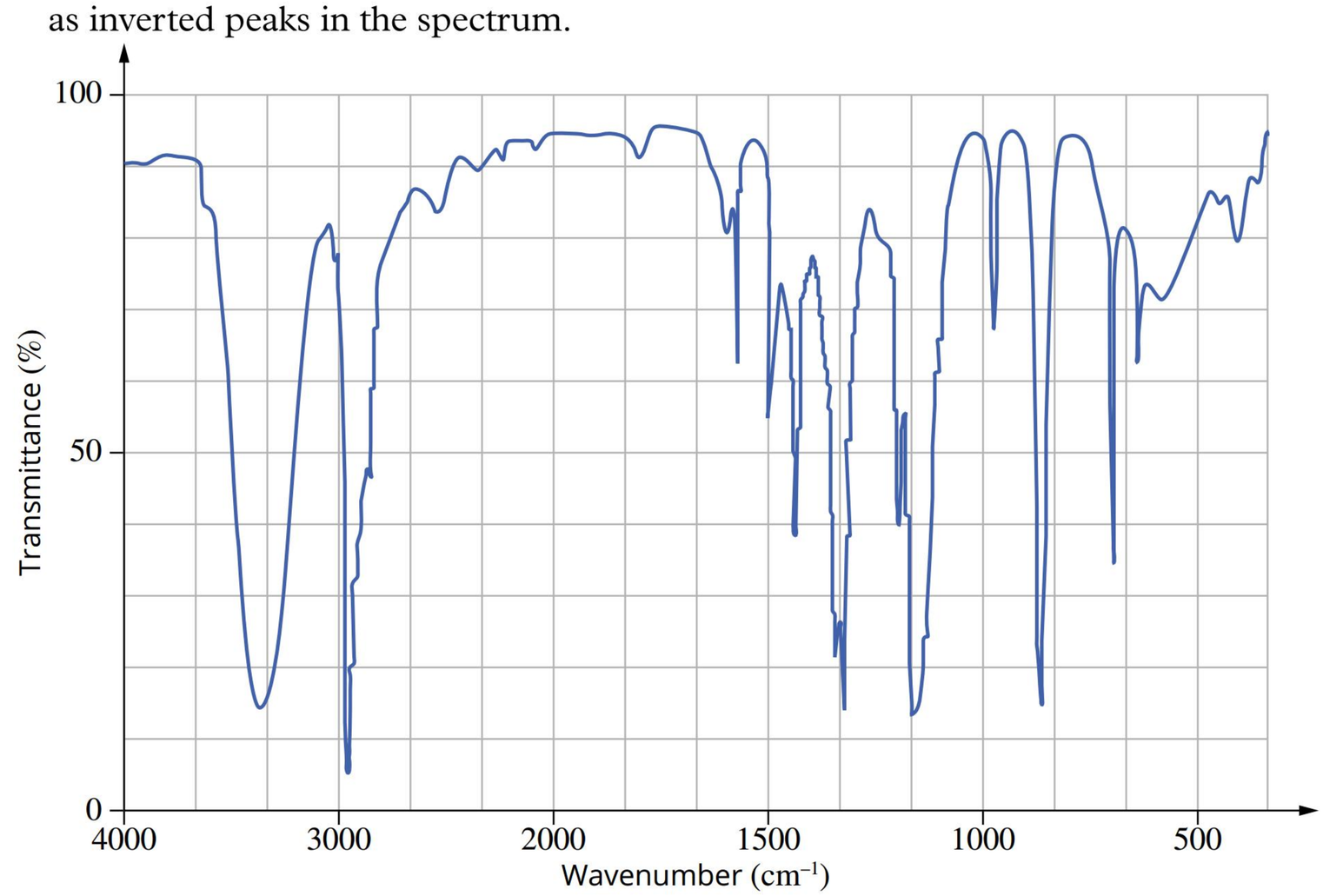


FIGURE 11.4.6 The infrared spectrum of 2-methylpropan-2-ol

Different terms can be used to describe absorption bands in IR spectra. Narrow absorption bands span only a few wavenumbers, whereas broader bands span between tens and hundreds of wavenumbers. Absorption bands are also described as 'strong', 'medium' or 'weak' if they absorb a large, moderate or small amount of radiation, respectively (Figure 11.4.7).

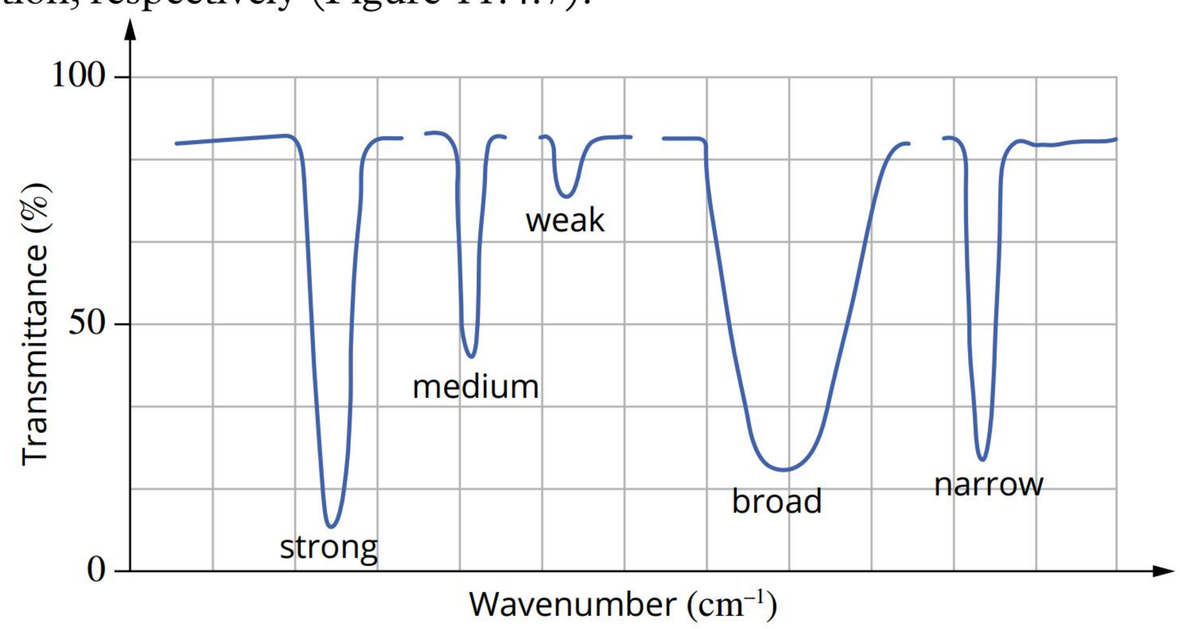


FIGURE 11.4.7 Descriptions used for different shapes and strengths of infrared absorption bands

Absorption bands above about 1400 cm^{-1} are used to identify functional groups (discussed in Chapter 8) because this region coincides with the energy associated with the characteristic stretching vibrations of the atoms in these groups. The region below 1400 cm^{-1} is called the **fingerprint region** because absorption bands of this frequency tend to be unique to each compound. If a known compound and an unknown compound have the same absorption spectrum below 1400 cm^{-1}, they are almost certainly the same.

Interpreting infrared spectra

Each type of bond absorbs IR radiation over a typical range of wavenumbers. For example, it takes energy in the 2720–3100 cm^{-1} region to stretch a C–H bond, and energy in the 750–1100 cm^{-1} region to stretch a C–C bond. The characteristic regions of absorption for different bonds in an IR spectrum are shown in Figure 11.4.8.

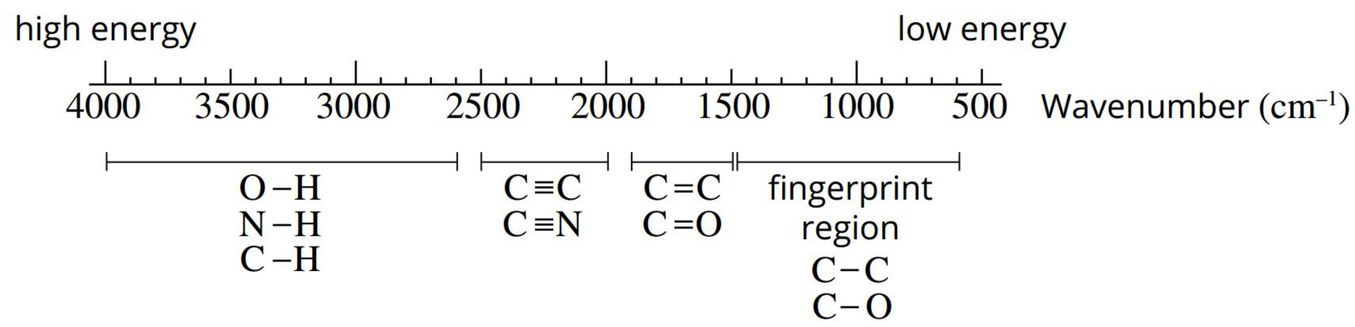


FIGURE 11.4.8 Typical regions for absorption bands from different bonds in the infrared spectrum

When chemists look at the IR spectrum of an unidentified organic compound, they often refer to tables and charts showing the wavenumbers at which the main functional groups absorb. This can give broad clues to the bond types and functional groups present in the molecule. For positive identification, the entire spectrum of an unidentified compound can be compared to a database of spectra, often containing tens of thousands of spectra of known compounds.

The characteristic range for IR absorptions of common functional groups is summarised in Table 11.4.3. These values are provided in the Senior Chemistry Formula and Databook.

TABLE 11.4.3 Characteristic range of infrared absorption due to stretching in organic molecules

Bond	Wavenumber (cm^{-1})
C–I	490–620
C–Br	500–600
C–Cl	600–800
C–F	1000–1400
C–O (alcohol, ester)	1050–1410
C=C (alkenes)	1620–1680
C=O (aldehydes, acids, esters, ketones)	1700–1750
C≡C	2100–2260
O–H (carboxylic acids)	2500–3000
C–H (alkanes, alkenes, alkynes, aldehydes, amides)	2720–3100
O–H (alcohols)	3200–3600
N–H (primary amines)	3300–3500

IR spectroscopy can be useful for distinguishing between very similar compounds. Consider the molecules propanoic acid and methyl ethanoate. These two compounds are isomers with the molecular formula $C_3H_6O_2$. The IR spectra of the compounds, shown in Figure 11.4.9, have some features in common and some differences. Both spectra have an absorption band at about 1700 cm^{-1} due to the stretching of the carbonyl (C=O) bond.

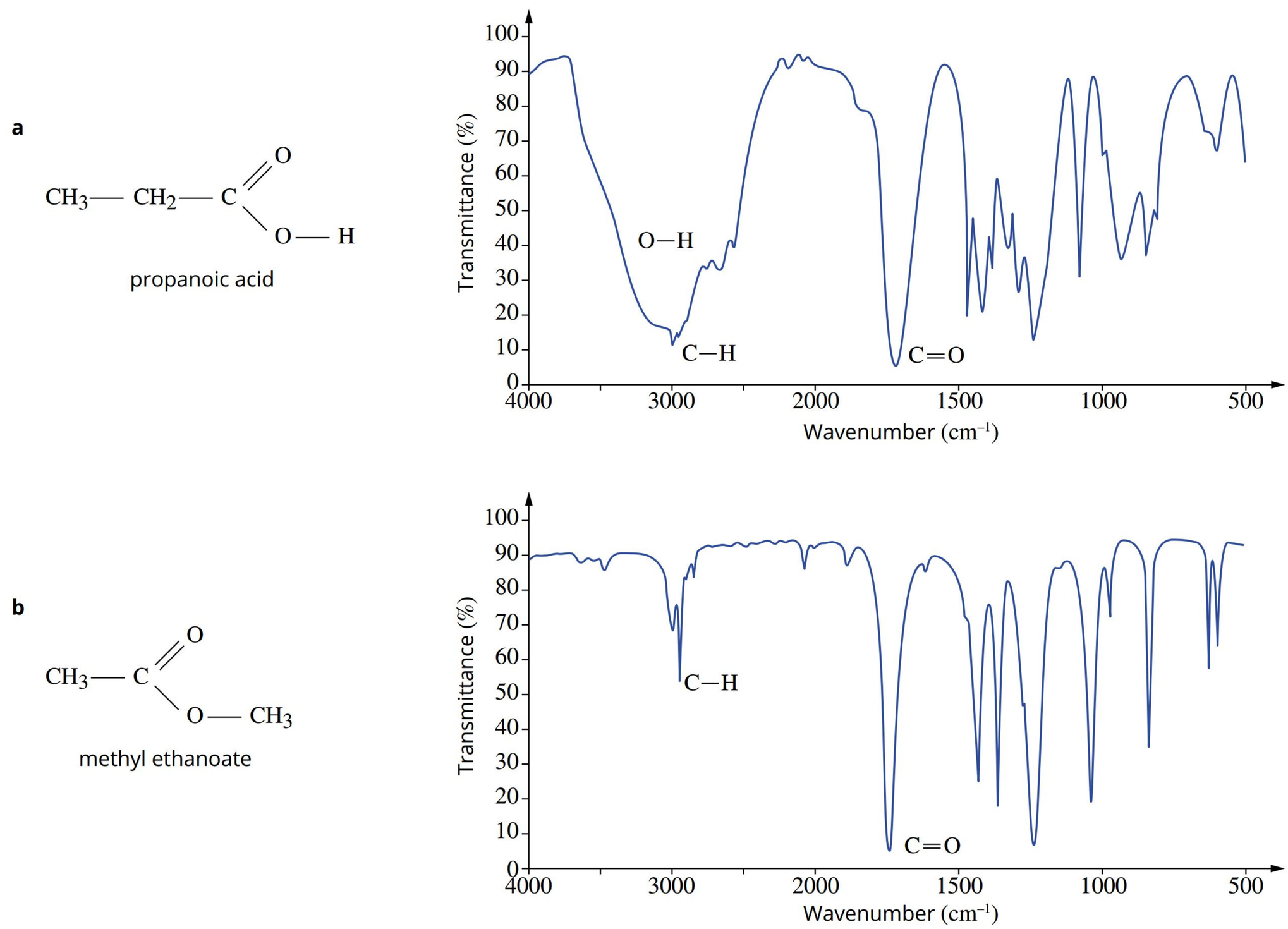


FIGURE 11.4.9 Infrared spectra of (a) propanoic acid and (b) methyl ethanoate

In methyl ethanoate, the narrow absorption band at around 3000 cm^{-1} is due to the C–H bonds in the two methyl groups as seen in the structural formula.

In propanoic acid, the broad absorption band from 2700 cm^{-1} to 3600 cm^{-1} is due to the O–H bond found in a carboxylic acid. This broad absorption band partly masks the absorption due to C–H bonds that are also present in this spectrum.

In this way, the data in Table 11.4.3 can be used to identify the bonds that are likely to be present in an unidentified compound from their characteristic absorption bands. This information allows you to determine which of the main functional groups are present. The IR spectrum may also be used to prove that a functional group is not present, helping you to narrow down the possible structure of the compound.

Some key considerations when interpreting infrared spectra of organic molecules in this course of study are:

- Absorption bands can overlap and/or can be 'hidden' by other absorbance bands. Look closely at Figure 11.4.9. The C–H band at 3000 cm^{-1} is only partially visible in (a) compared to (b) due to overlap with the large and wide O–H band.

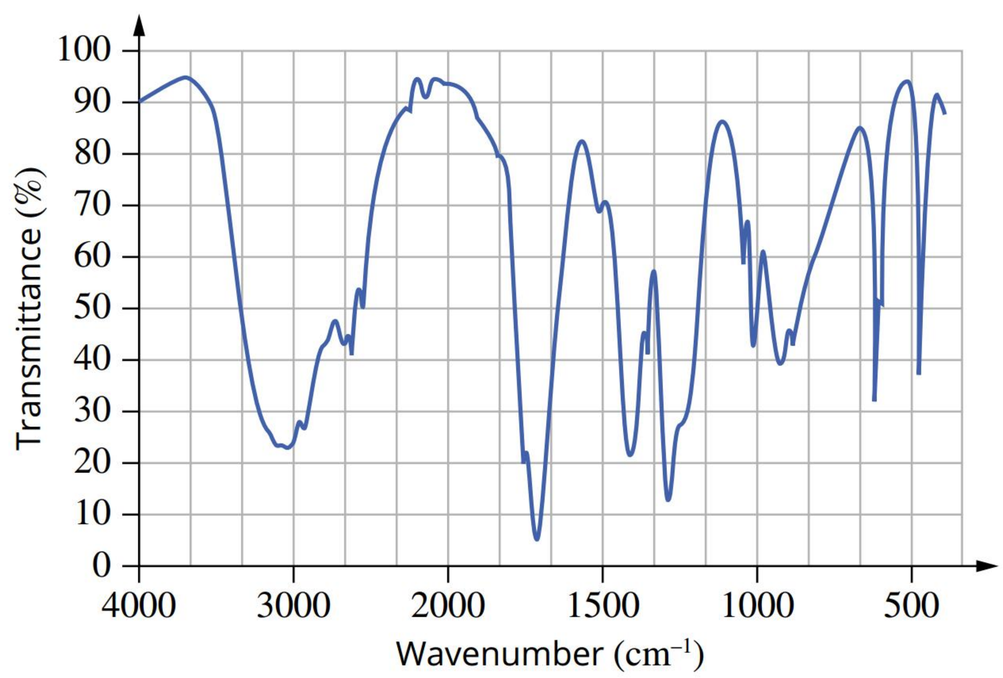
- There are multiple bands in the fingerprint region (less than 1400 cm^{-1}), and so the identification of these bonds, individually, is difficult. We compare the overall pattern in this range of wavelengths to a known standard or database, rather than identifying individual bands.
- The OH functional group absorption band is a distinctive, broad (wide) one. However, we see that the band has a different wavenumber in alcohols (3200–3600 cm^{-1}) compared to carboxylic acids (2500–3000 cm^{-1}).

Different types of covalent bonds absorb IR radiation within a characteristic range of frequencies (wavenumbers), allowing the functional groups in an organic compound to be identified.

Worked example 11.4.1

USING AN IR SPECTRUM TO IDENTIFY AN UNKNOWN COMPOUND

Use the IR spectrum of an unknown compound to identify the functional groups present and thus determine its identity. The molecular formula of the compound is $C_2H_4O_2$. You will need to refer to the IR absorption data in Table 11.4.3 on page 487.

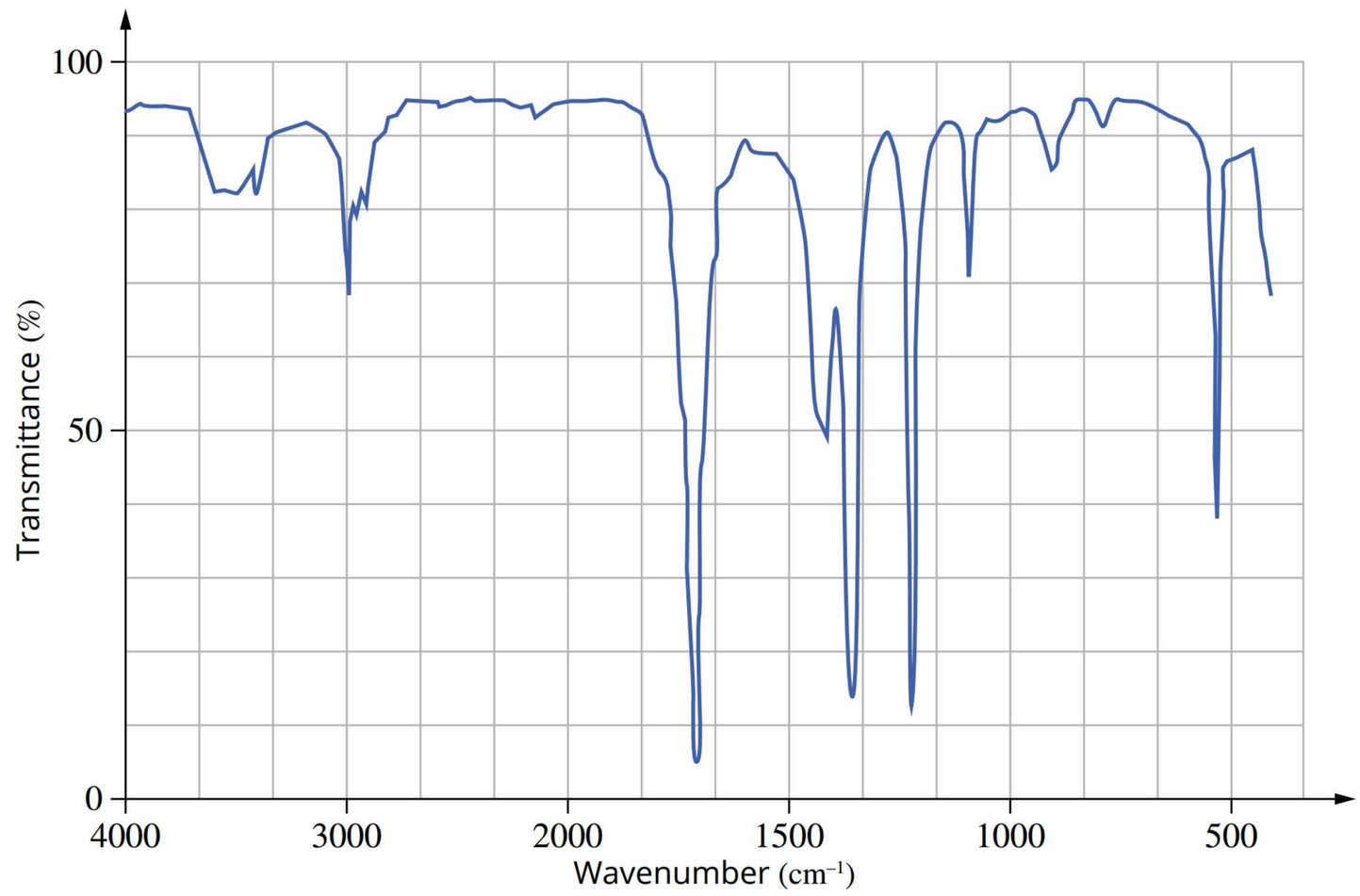


Thinking	Working
Identify any absorption bands that correspond to the absorption bands of bonds in the IR absorption data table.	There is a strong, narrow band at approximately 1700 cm^{-1}, which corresponds to the absorption by a carbonyl, C=O, group. The broad band centred at about 3000 cm^{-1} corresponds to the absorption by the O–H bond of a carboxylic acid.
Identify the functional group or groups that are present.	The spectrum shows absorption bands corresponding to the presence of C=O and carboxylic acid O–H bonds. This suggests the presence of a carboxyl functional group, –COOH. This means that CO_2H is used from the unidentified compound $C_2H_4O_2$, which leaves CH_3. From the formula and IR spectrum, it can be concluded that the compound is ethanoic acid (CH_3COOH).

➤ Try yourself 11.4.1

USING AN IR SPECTRUM TO IDENTIFY AN UNKNOWN COMPOUND

Use the IR spectrum of an unknown compound to identify the functional groups present and thus determine its identity. The molecular formula of the compound is C_3H_6O. You will need to refer to the IR absorption data in Table 11.4.3 on page 487.



11.4 Review

SUMMARY

- Organic compounds interact with electromagnetic radiation in different ways depending on the energy of the radiation.
- Different types of covalent bonds absorb IR radiation within a characteristic range of frequencies (wavenumbers), allowing the functional groups in an organic compound to be identified.
- Each compound has a unique absorbance pattern in the fingerprint region of the IR spectrum, and this can be used to identify the compound.

KEY QUESTIONS

Describe

1 Identify which absorption bands would you expect to see from the following functional groups.

a hydroxyl
b amide
c amine
d carboxyl
e ester
f ketone

2 Define the terms 'absorption bands' and 'fingerprint region.'

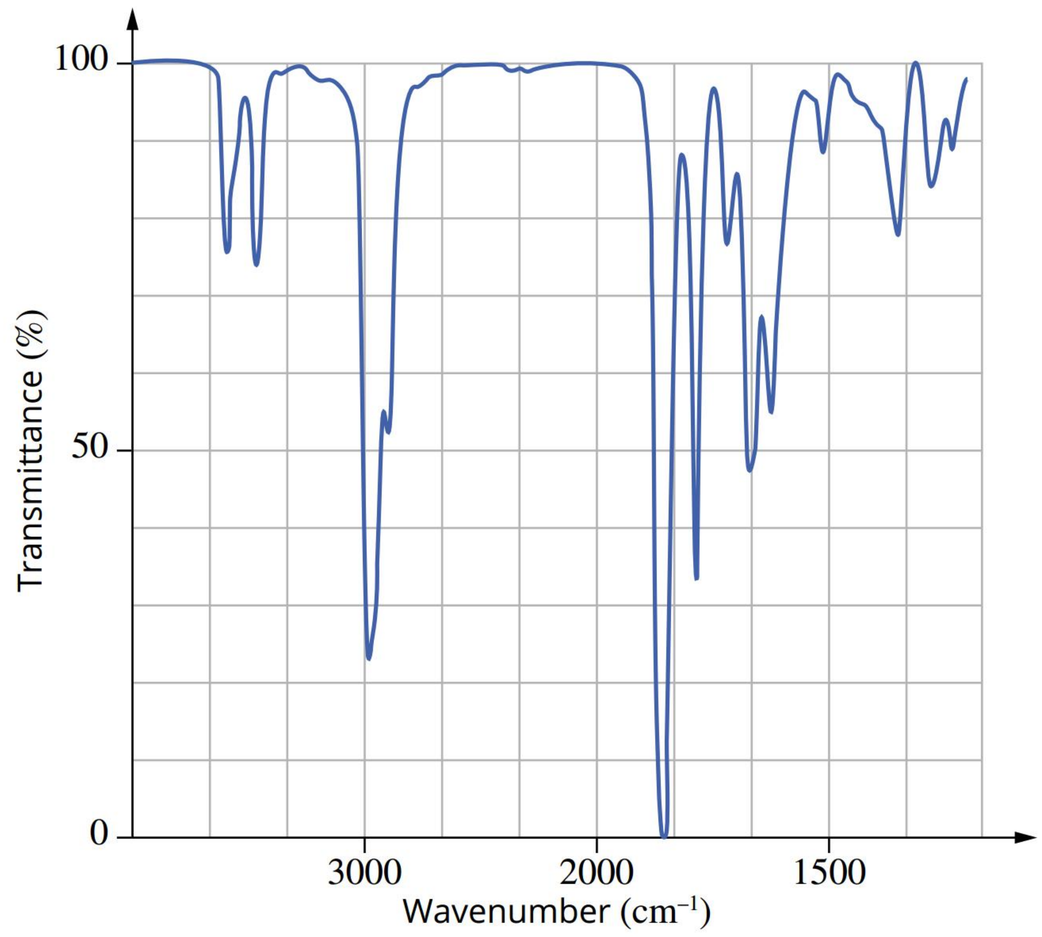
3 Describe the changes that occur in molecules upon the absorption of infrared radiation.

Apply

4 Determine which of the following compounds would show or not show a broad peak at around 3000 cm^{-1}. propan-1-ol, propan-2-ol, ethane, ethanol, ethanoic acid, methanoic acid, ethyl ethanoate, butanoic acid, 1-chloroethane and methyl-1-amine (an amine with one carbon)

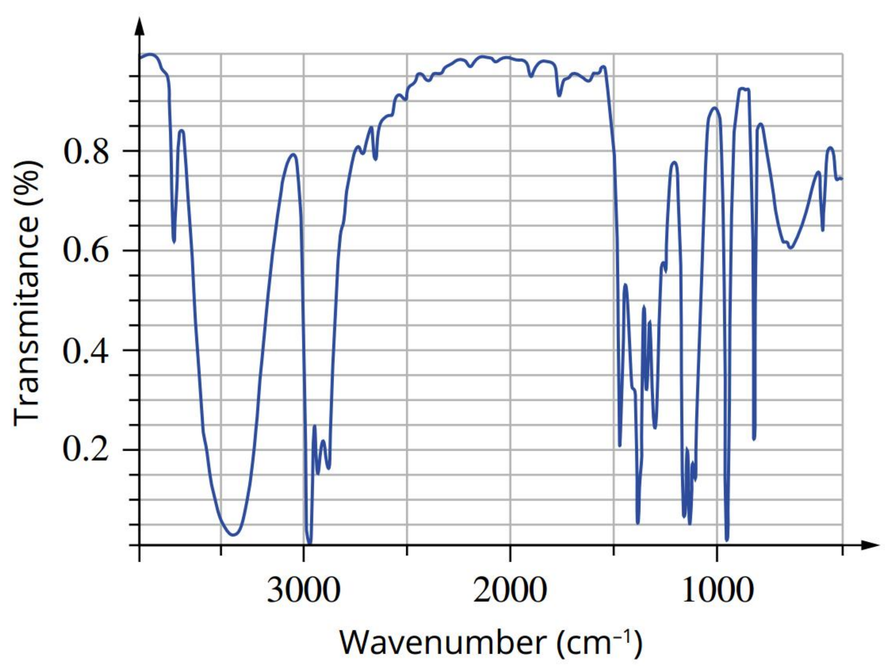
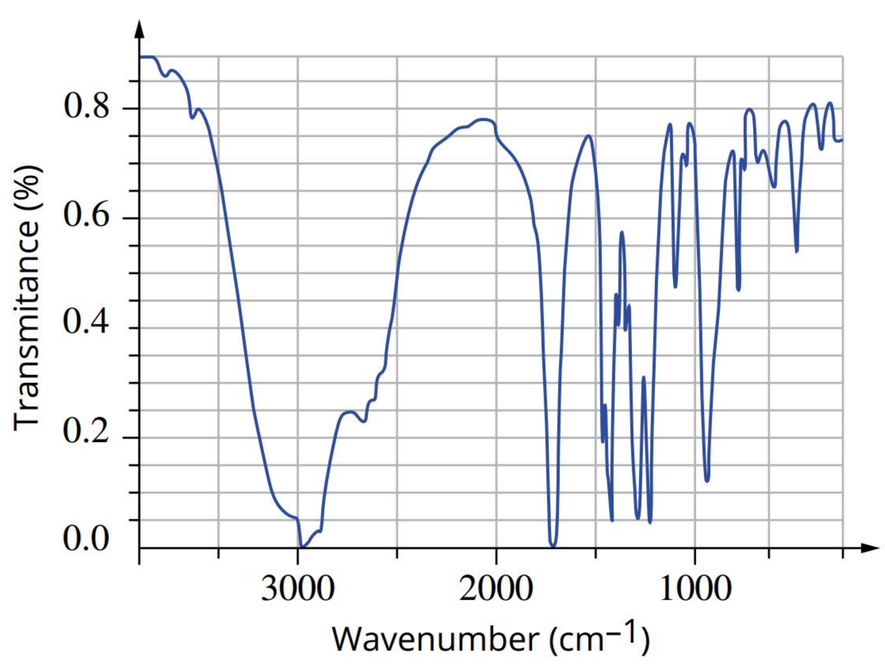
5 Explain why the absorption bands due to C–O and C–C bonds are often of little help when determining the structure of an unidentified compound, but are valuable in the confirmation of the identity of a known compound.

6 Use the following infrared spectrum of an unidentified compound to identify the functional groups present. The molecular formula of the compound is C_3H_5NO.



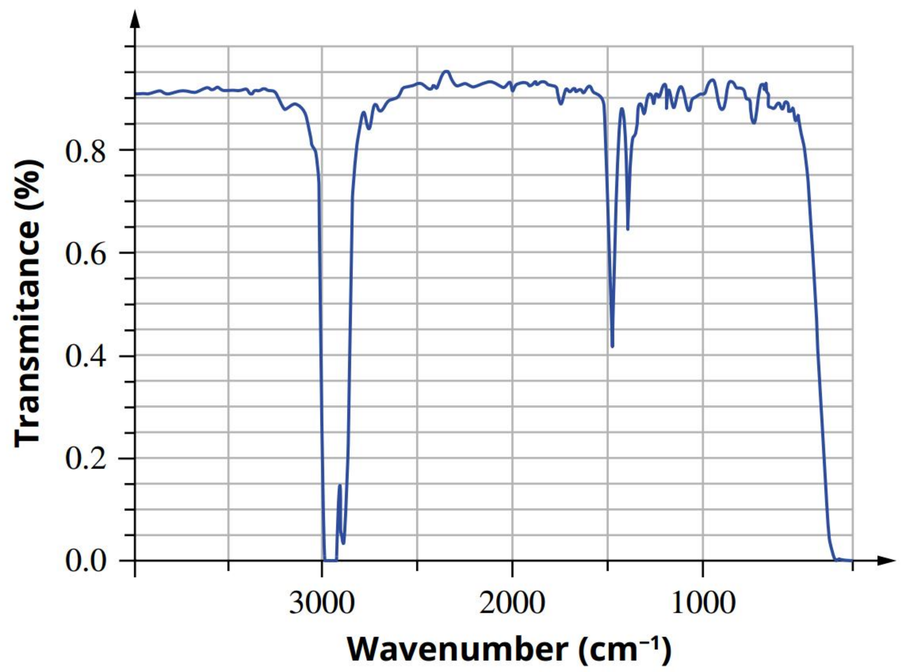
Analyse

7 For each of the following IR spectra, select the correct name of the organic compound from the alternatives provided.

	Spectrum	Possible names of the organic compound
a		**A** propene **B** propan-2-ol **C** propanoic acid **D** propanal
b		**A** butan-1-ol **B** but-2-one **C** butanamide **D** butanoic acid

Continued over page

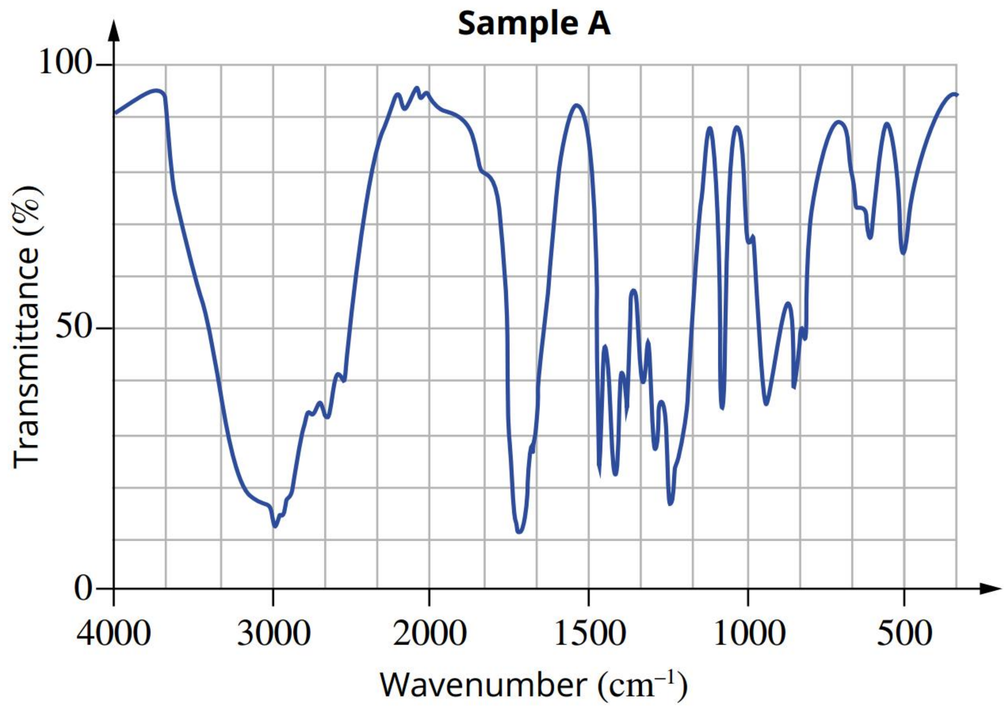
11.4 Review *continued*

c		**A** hexan-3-ol **B** hexane **C** hexanoic acid **D** hex-1-ene

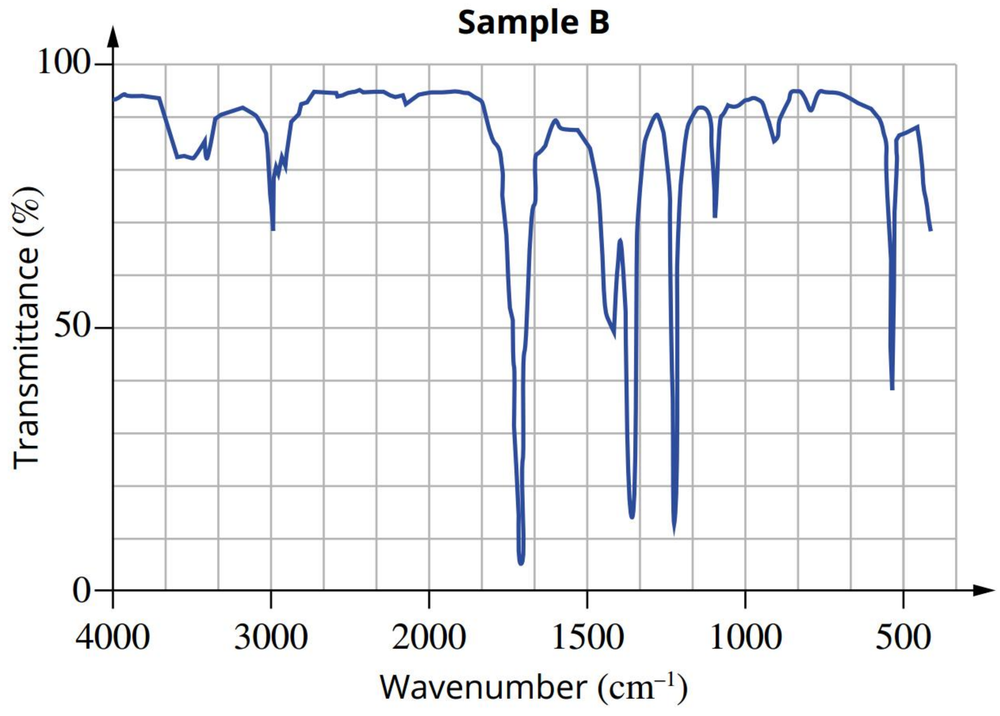
8 A careless laboratory assistant placed solutions of propanoic acid and propanone in unmarked containers. The laboratory assistant decided to analyse small samples of the unknown solutions using IR spectroscopy, and labelled the unknown solutions as sample A and sample B.

Identify the two unknown solutions using chemical formulas and the following IR spectra.

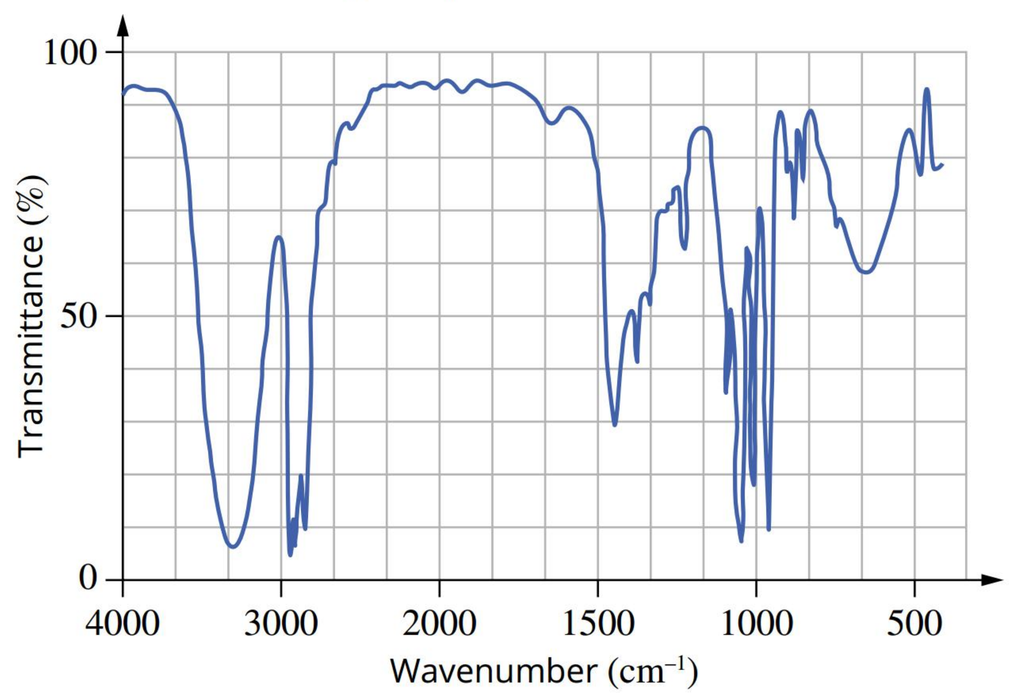
Sample A



Sample B



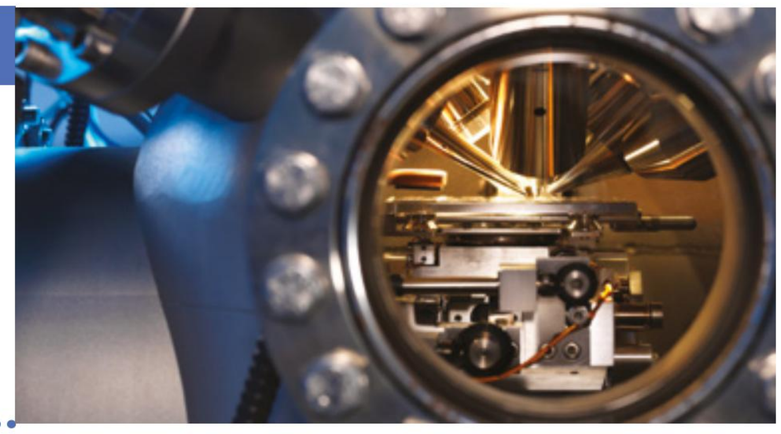
9 Champagne and wine are made by the fermentation of glucose ($C_6H_{12}O_6$) obtained from grapes. During glucose fermentation, ethanol and carbon dioxide are produced. If the alcohol is left to oxidise, sour-tasting ethanoic acid (vinegar) may form. Explain how the IR spectrum below can be used to confirm that no ethanoic acid is present, and that the product is ethanol. The aqueous solution formed was analysed by IR spectroscopy, and the following IR spectrum was obtained. Identify the product in the solution.



11.5 Spectral analysis of organic compounds

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- determine the structural, empirical and molecular formula of an unidentified compound by using spectral analysis
- state the importance of employing a range of analytical techniques
- combine mass spectrometry and IR spectroscopy to identify an organic compound.



Chemists determine the structure and identity of unknown compounds by employing a range of analytical techniques. Each technique provides a different piece of information about the compound's structure, which, when considered together (along with educated guesses), can identify the substance. The process can be compared to putting together the pieces of a jigsaw puzzle.

The structures of organic compounds are often determined using a combination of IR spectroscopy and mass spectrometry. Chemical and physical properties can also provide clues about the identity of a compound. The atomic mass spectrum provides information for calculating the empirical formula, whereas the molecular mass spectrum provides information for calculating the molecular formula.

In this module, you will investigate how the structure of an unidentified compound can be determined.

As you read through and complete the questions in this section, you will need to refer to Table 11.4.3 on page 487.

Figure 11.5.1 is a useful guide to follow when working through these problems.

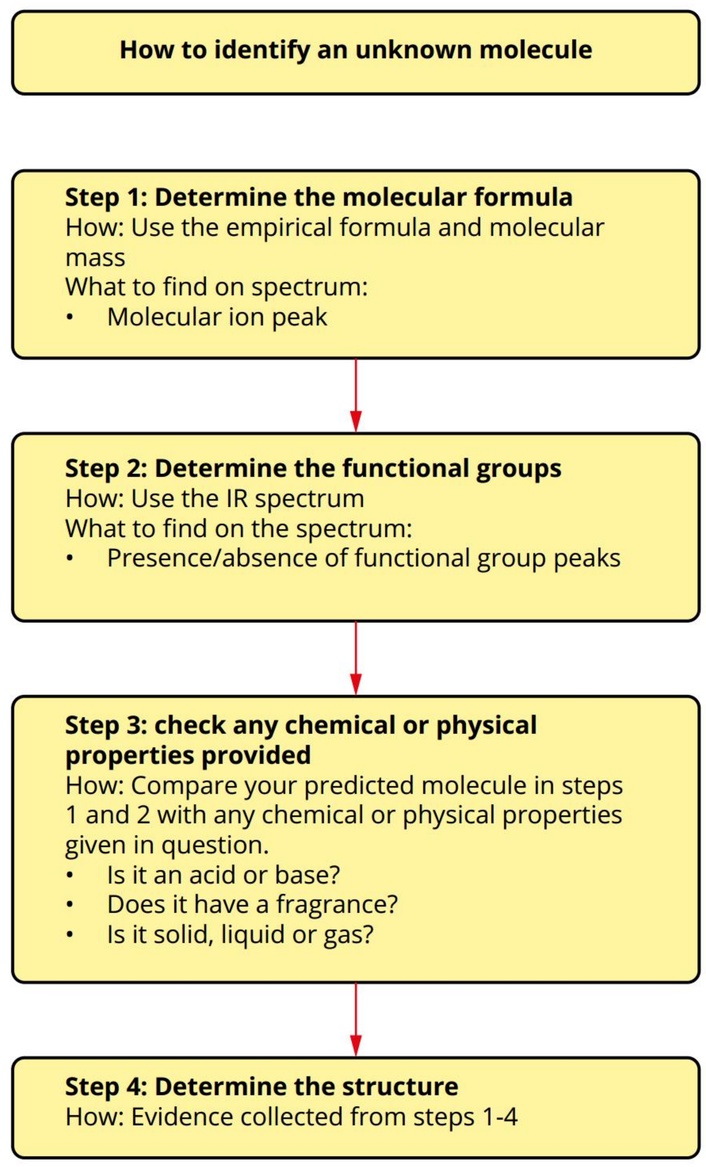


FIGURE 11.5.1 Flow chart listing the general steps used to identify an unknown molecule

COMBINING ANALYTICAL TECHNIQUES

Ethanol (C_2H_5OH) will be used as an example of how the results of different types of analysis can be used to identify an unknown organic compound. Ethanol has a molar mass of $46\,g\,mol^{-1}$. The structural formula of ethanol is shown in Figure 11.5.2.

The mass spectrum for ethanol can be seen in Figure 11.5.3. Using this spectrum, the following can be determined.

- There is a molecular ion peak at $m/z = 46$, which corresponds to a relative molecular mass of 46.
- The fragment ion peaks are identified on the spectrum and are consistent with the fragmentation of a molecule with the formula $C_2H_6O^+$.

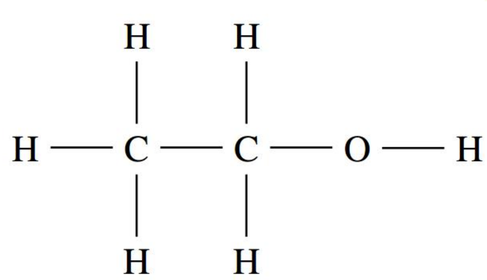


FIGURE 11.5.2 Structural formula for ethanol

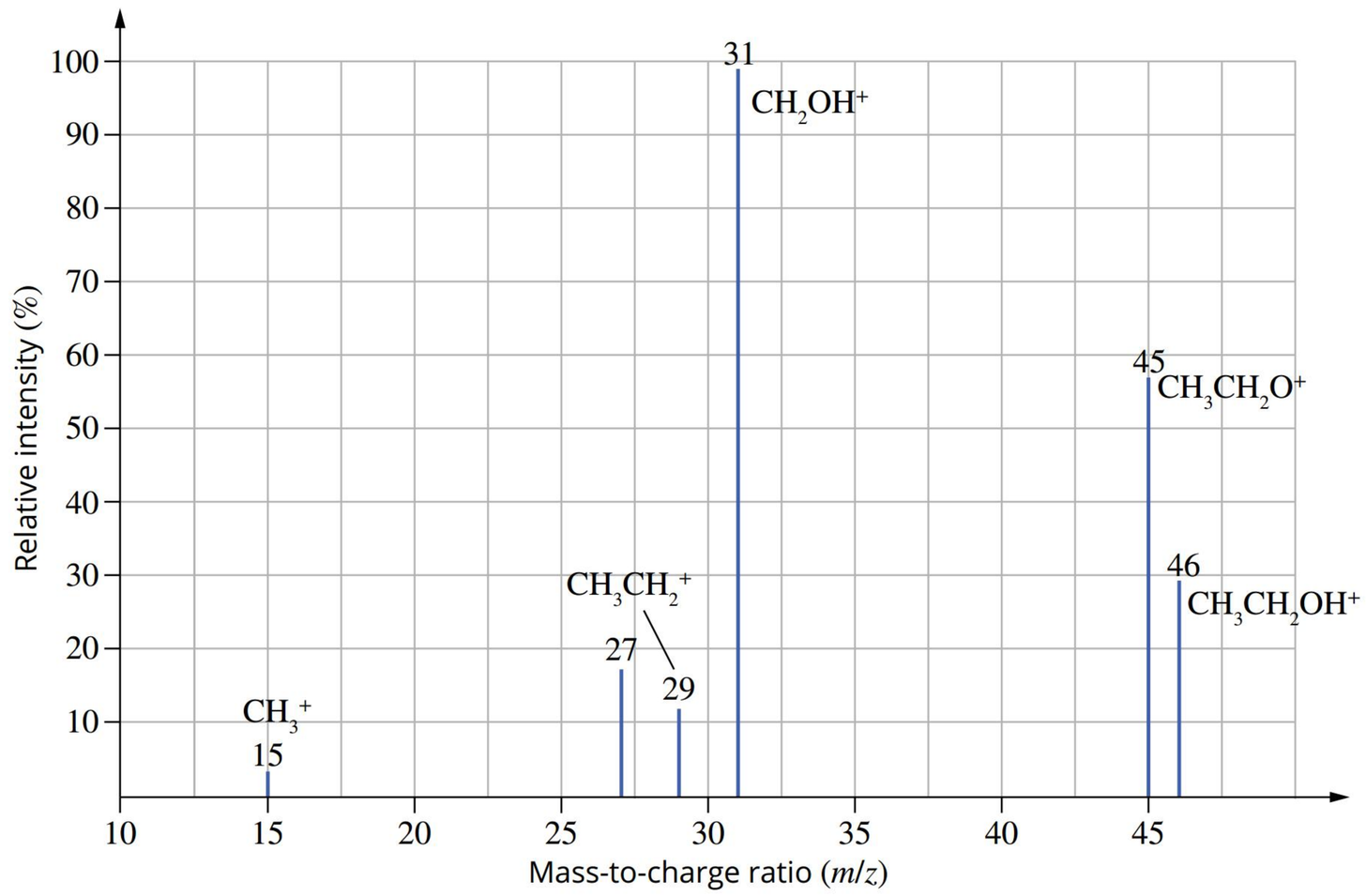


FIGURE 11.5.3 Mass spectrum of ethanol

The infrared spectrum of ethanol, shown in Figure 11.5.4, provides the following information.

- The most prominent feature is the broad stretch at 3200–3600 cm^{-1} due to the O–H bond and confirms the presence of an alcohol hydroxyl group.
- The absorption bands due to the C–H and C–O bonds are also shown.

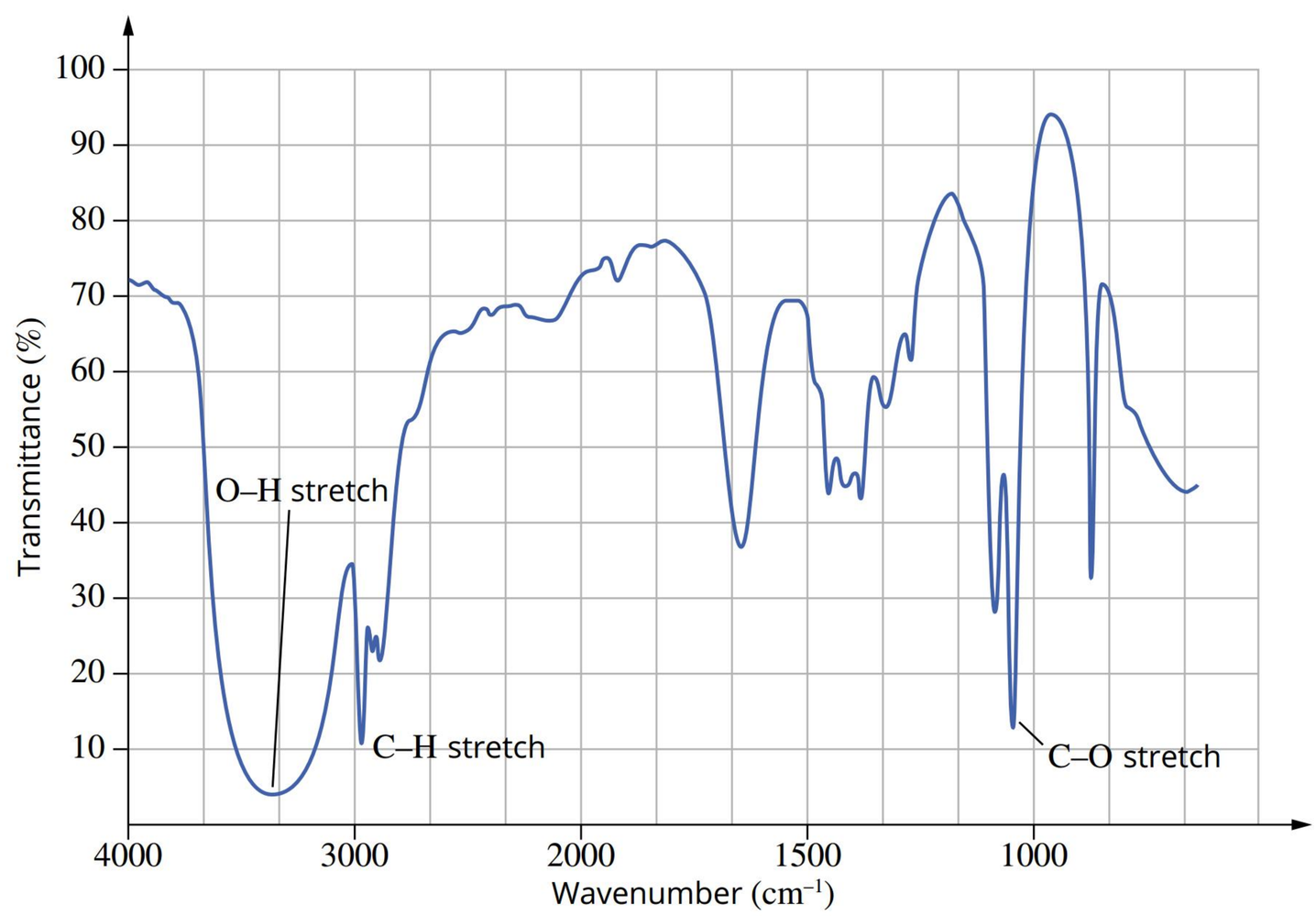


FIGURE 11.5.4 IR spectrum of liquid ethanol

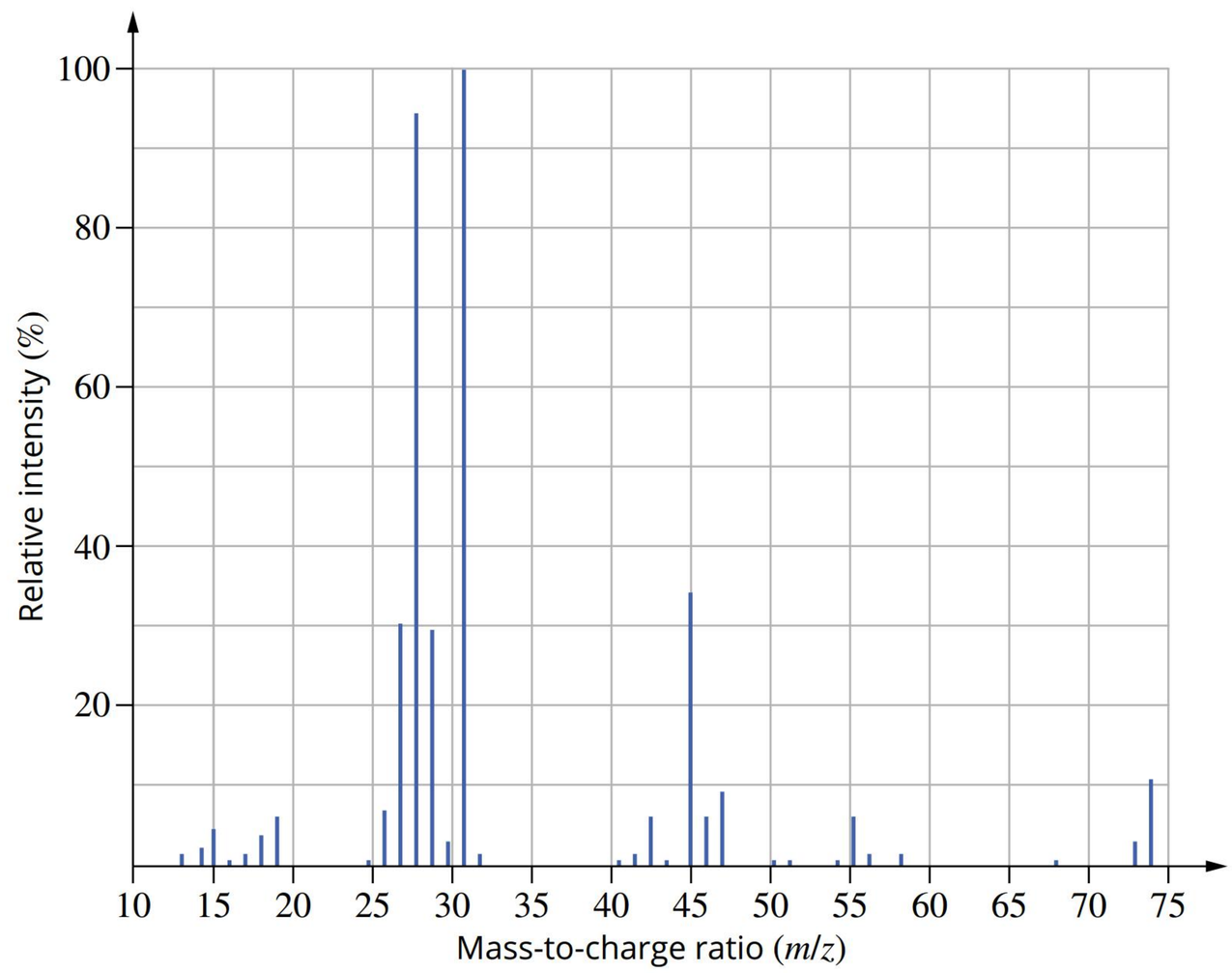
When each piece of evidence from analysing the different spectra is put together, you can see that the structure must be CH_3CH_2OH. Each of the spectra contains the peaks expected of ethanol, and none of the spectra contains information that is inconsistent with ethanol.

Worked example 11.5.1

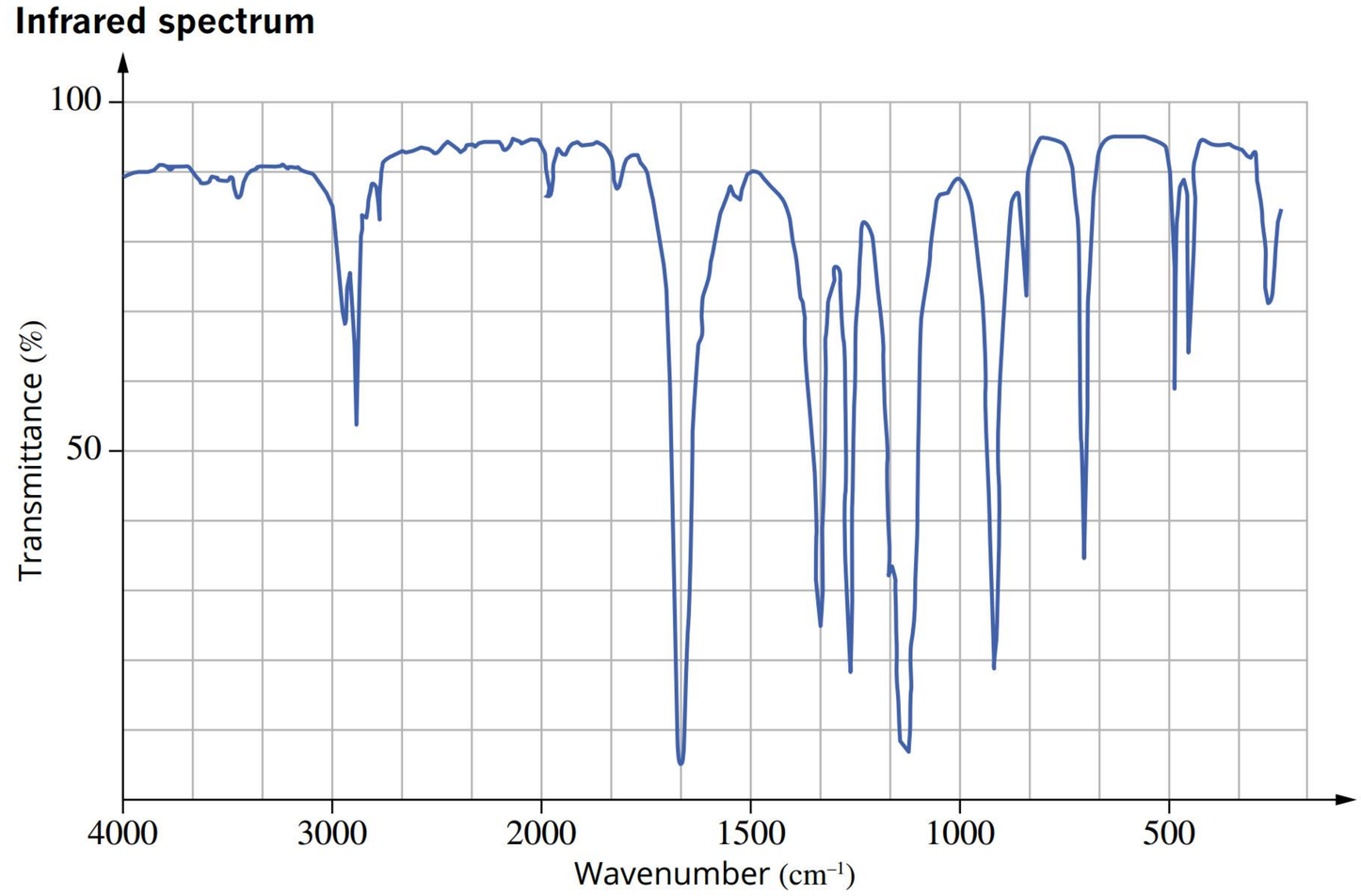
DETERMINING MOLECULAR STRUCTURE FROM SPECTRAL ANALYSIS

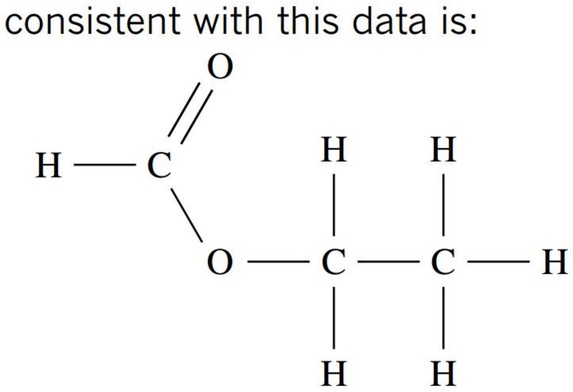
A sweet-smelling liquid was synthesised in the laboratory. Chemical tests show that the compound is not an aldehyde or a ketone. Chemical analysis shows that it is 48.64% carbon, 8.16% hydrogen and 43.20% oxygen. Use this information and the mass and IR spectra provided to deduce the structure and name of the compound.

Molecular mass spectrum



Infrared spectrum



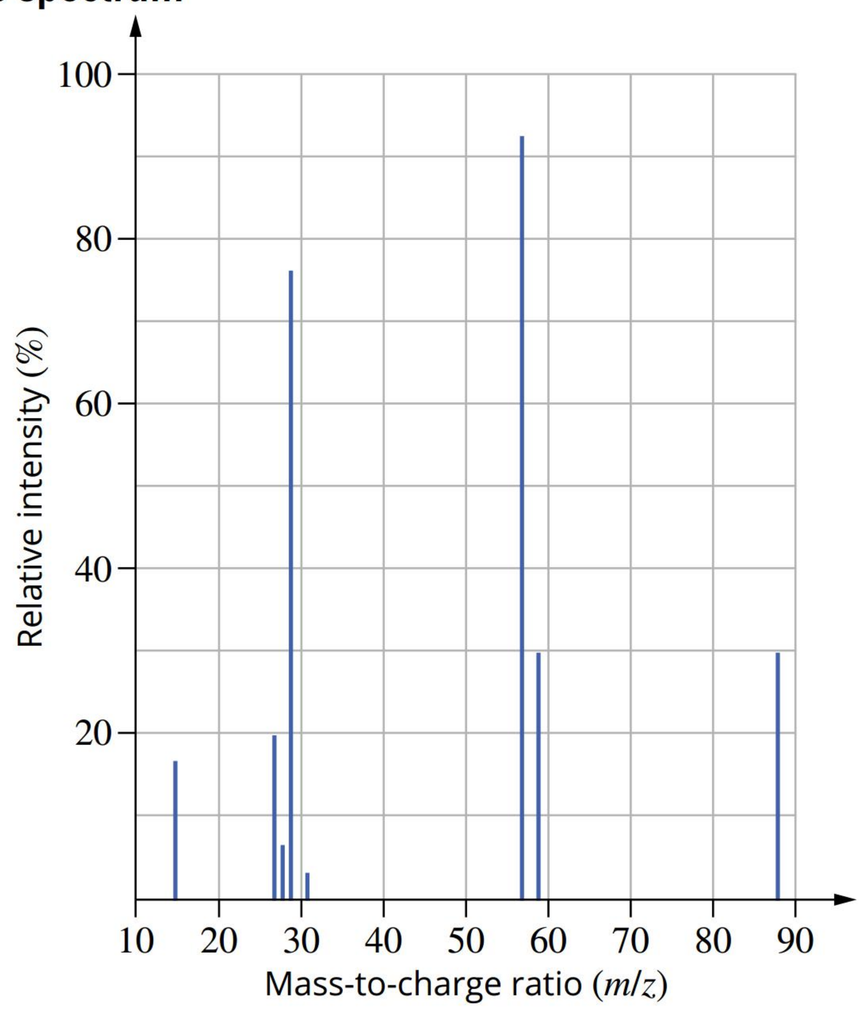
Thinking	Working
Use the percentage composition data to calculate the empirical formula.	Assume that you have a 100 g sample, so that the percentage values can become masses in grams. Calculate the amount, in mol, of each element in the compound. $n(\text{H}) = \frac{8.16}{1.01} = 8.08\,\text{mol}$ $n(\text{C}) = \frac{48.64}{12.01} = 4.05\,\text{mol}$ $n(\text{O}) = \frac{43.20}{16.00} = 2.70\,\text{mol}$ Simplify the mole ratio to whole numbers: H : C : O Divide by 2.70 $\frac{8.08}{2.70} : \frac{4.05}{2.70} : \frac{2.70}{2.70}$ 2.99 : 1.50 : 1 Multiply by 2 6 : 3 : 2 Empirical formula: $C_3H_6O_2$
Use the molecular mass spectrum to identify the molecular ion and relative molecular mass (refer to Table 11.3.1 on page 473).	The peak with the largest mass-to-charge ratio is at $m/z = 74$, so the relative molecular mass is 74 g mol^{-1}. This mass is consistent with the molecular formula of $C_3H_6O_2$. According to Table 11.3.1 on page 473, the peaks can be interpreted as follows: $m/z = 45$ correlates to $CH_3CH_2O^+$ or $COOH^+$ $m/z = 28$ correlates to CO^+
Use the IR spectrum to identify functional groups present in the compound (refer to Table 11.4.3 on page 487).	The IR spectrum shows a strong absorption band at 1700–1750 cm^{-1}, suggesting the presence of a C=O bond, and hence a carbonyl group. The IR spectrum does not contain a strong, broad absorption in the range of 2500–3000 cm^{-1}, indicating there is no O–H bond in the molecule.
Use the data from the spectra to deduce the structure of the compound. Name the compound.	The data provided by the spectra show that: • the empirical formula of the compound is $C_3H_6O_2$ • the molecular formula of the compound is $C_3H_6O_2$ • the mass spectrum of the compound shows peaks correlating to the following possible fragments: $CH_3CH_2O^+$ or $COOH^+$ and CO^+ • the IR spectrum of the compound shows the presence of a C=O, carbonyl group, but no hydroxyl group; therefore, the compound must be an ester with a methyl group attached. A structure consistent with this data is:  The predicted structure does not contain an aldehyde or ketone, as stated. Esters are sweet-smelling and are liquids (recall from Chapter 9). The compound must be methyl ethanoate.

➤ Try yourself 11.5.1

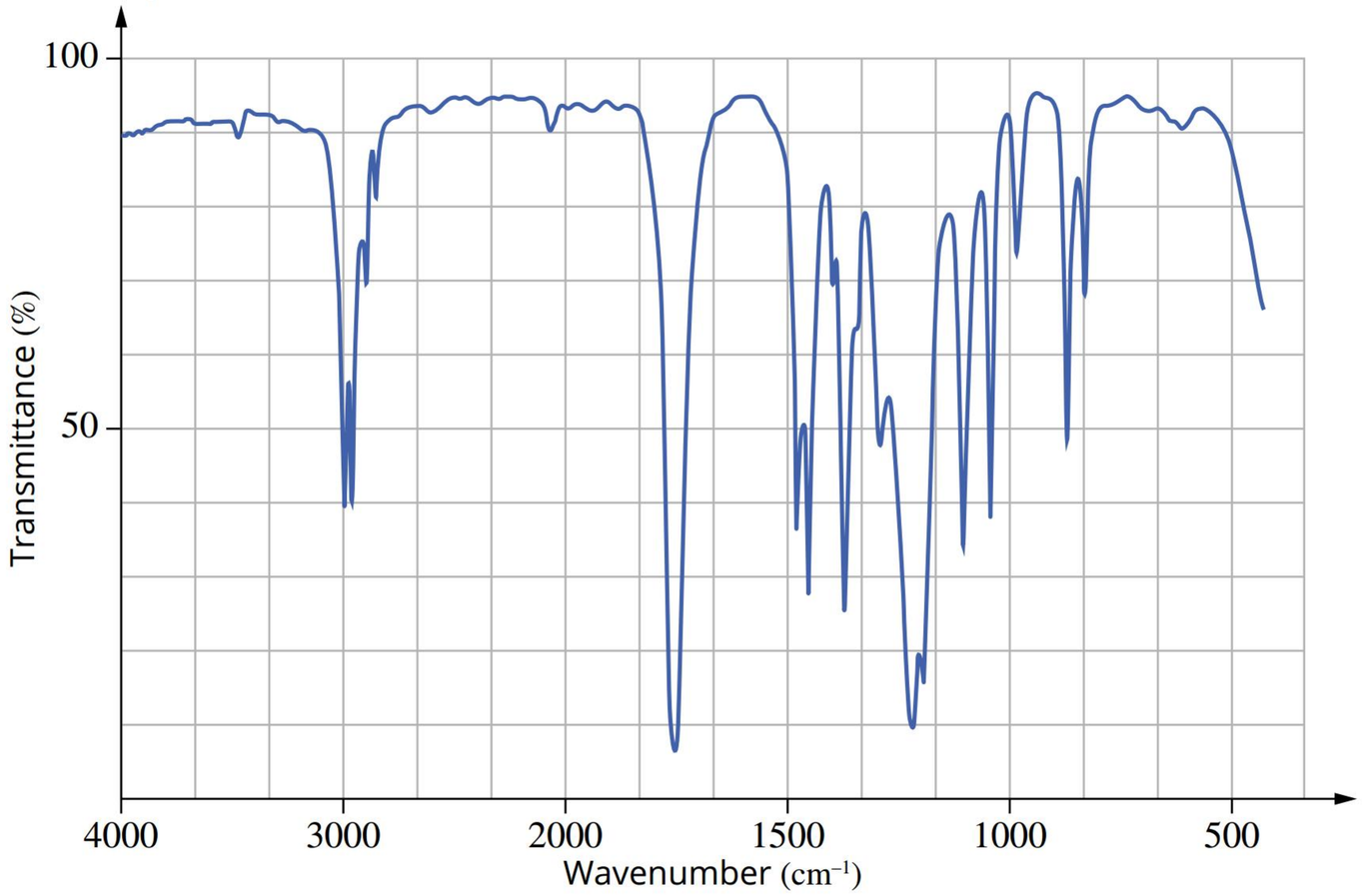
DETERMINING MOLECULAR STRUCTURE FROM SPECTRAL ANALYSIS

A student produced a sweet-smelling liquid. Chemical tests show that the compound is not an aldehyde or ketone. Chemical analysis shows that the compound is made up of 54.52% carbon, 9.17% hydrogen and 36.31% oxygen. Use this information and the mass and IR spectra provided to deduce the structure and name of the compound.

Molecular mass spectrum



Infrared spectrum



11.5 Review

SUMMARY

- A combination of information derived from mass spectrometry and infrared spectroscopy can be used to determine the structural, empirical and molecular formulas of organic compounds.
- The molecular formula can be determined from the information provided by the molecular mass spectrum (molecular mass) and the atomic mass spectrum (percentage composition and empirical formula).
- The infrared spectrum of a compound provides evidence about functional groups present in a molecule and can therefore identify the class of organic compound present.

KEY QUESTIONS

Describe

1 State which technique would be used to determine the functional groups in a sample.

2 You have a sample of a gas but are unsure whether it is ethane or propane. You have a choice of infrared spectroscopy or mass spectroscopy to identify the unknown gas. Name which technique will provide the most useful information you need to identify the gas and provide a reason for your selection.

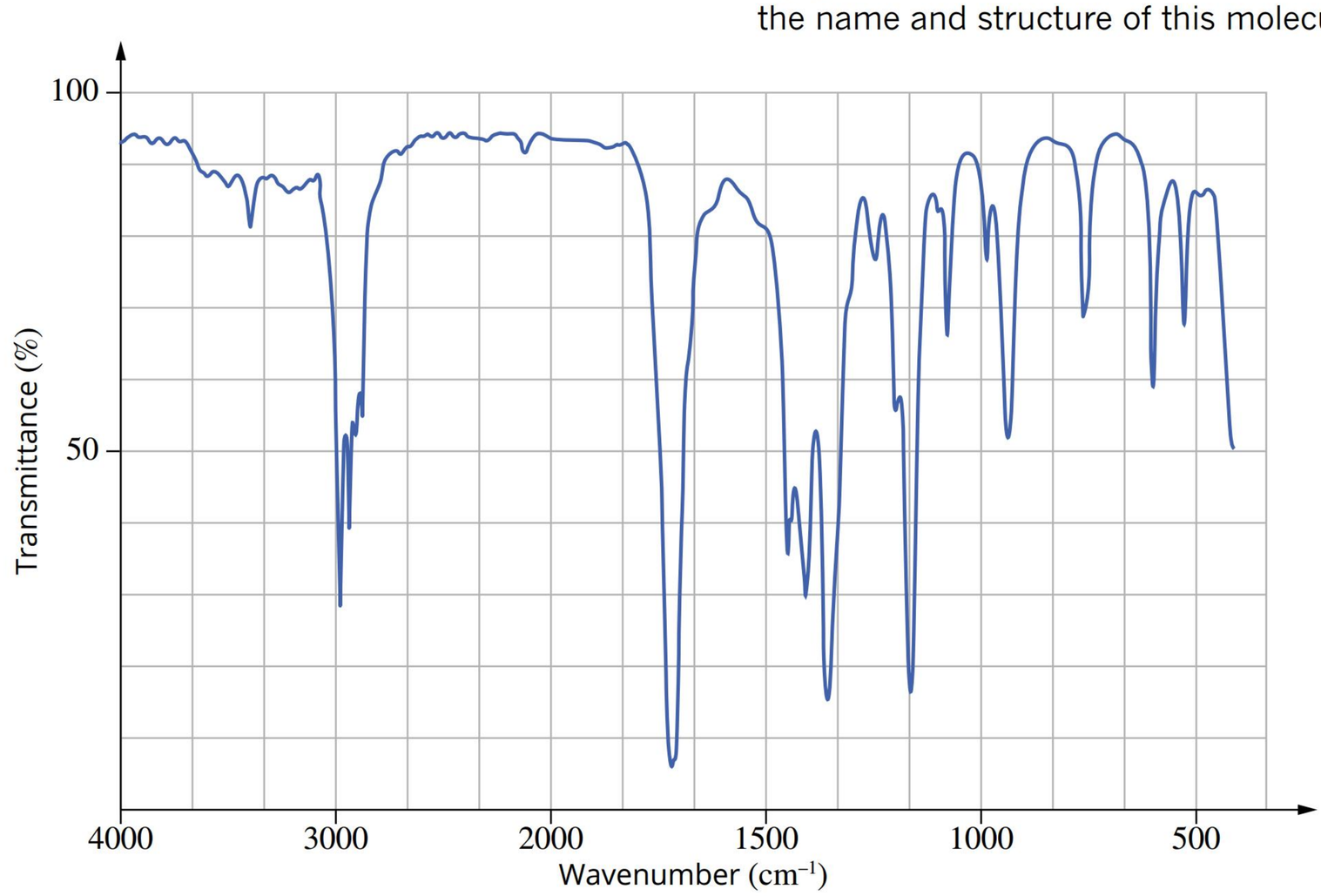
Apply

3 Explain the advantage of combining different analysis techniques.

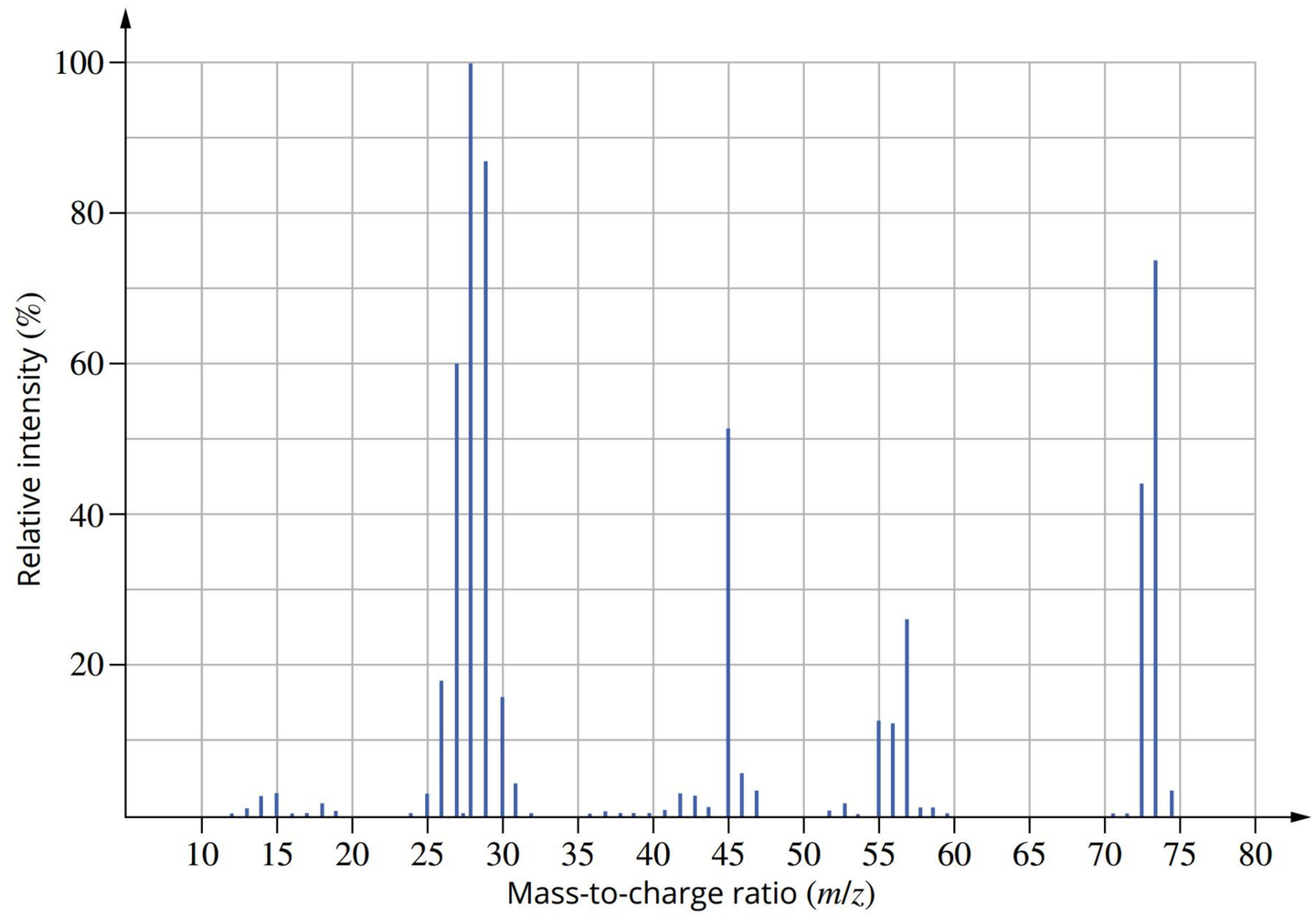
4 Explain why scientists cannot determine the unknown organic compounds in a mixture by simply looking at the IR or mass spectra.

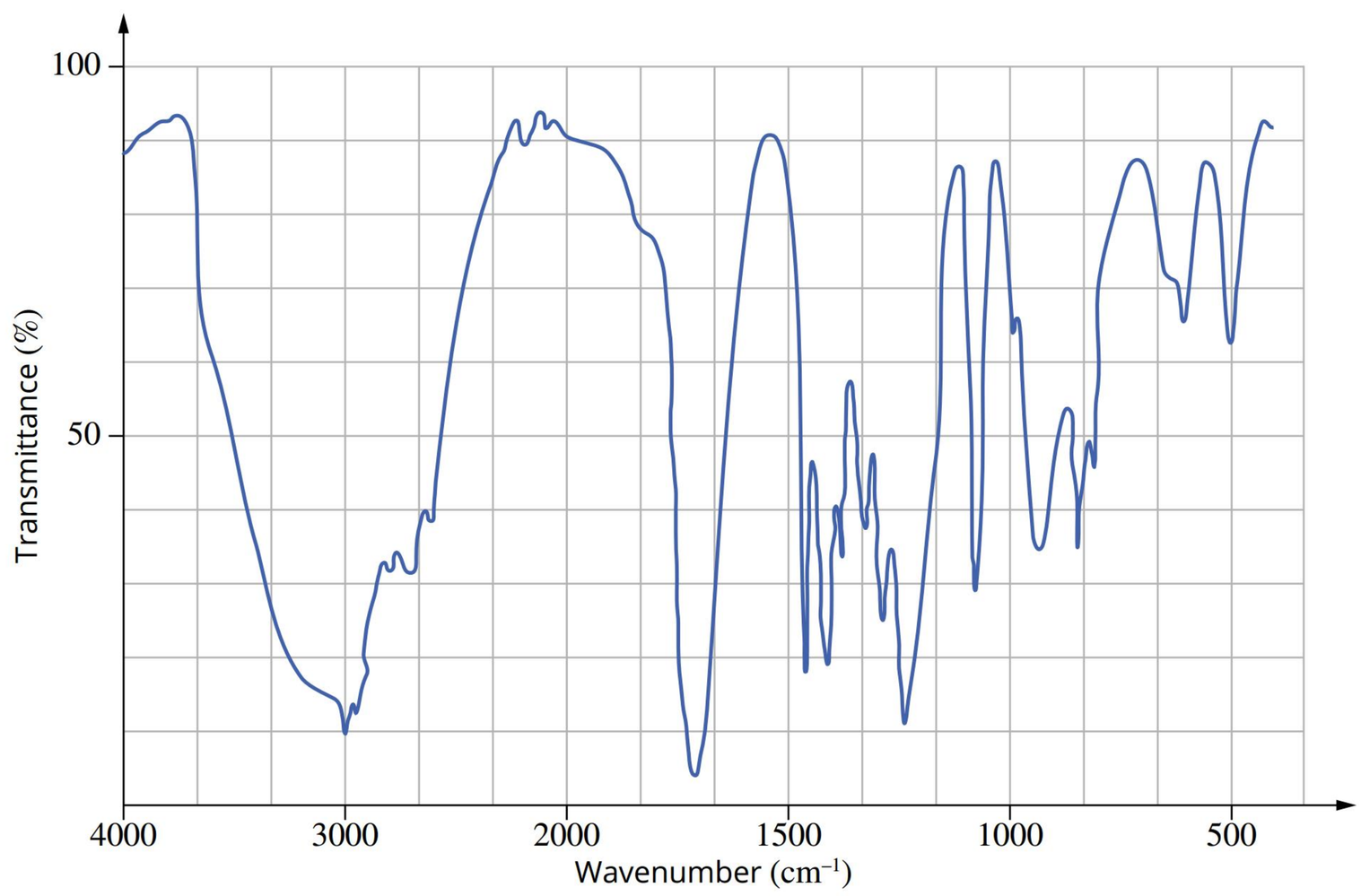
Analyse

5 An industrial solvent has the molecular formula C_4H_8O. Use the infrared spectrum below to determine the name and structure of this molecule.



6 An unidentified organic compound has an empirical formula of $C_3H_6O_2$. Determine the name of the compound using this information and the mass and IR spectra below.

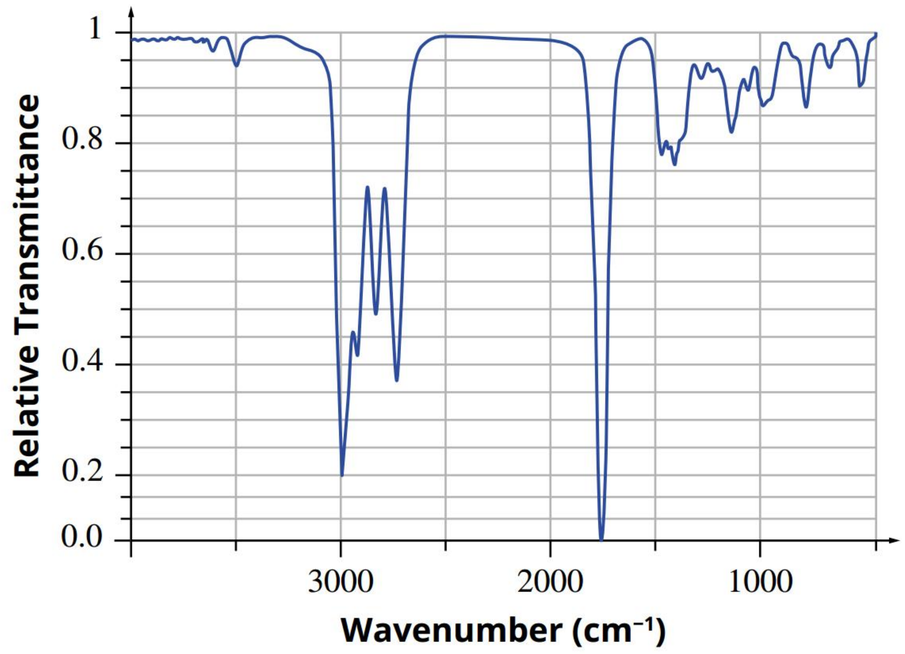


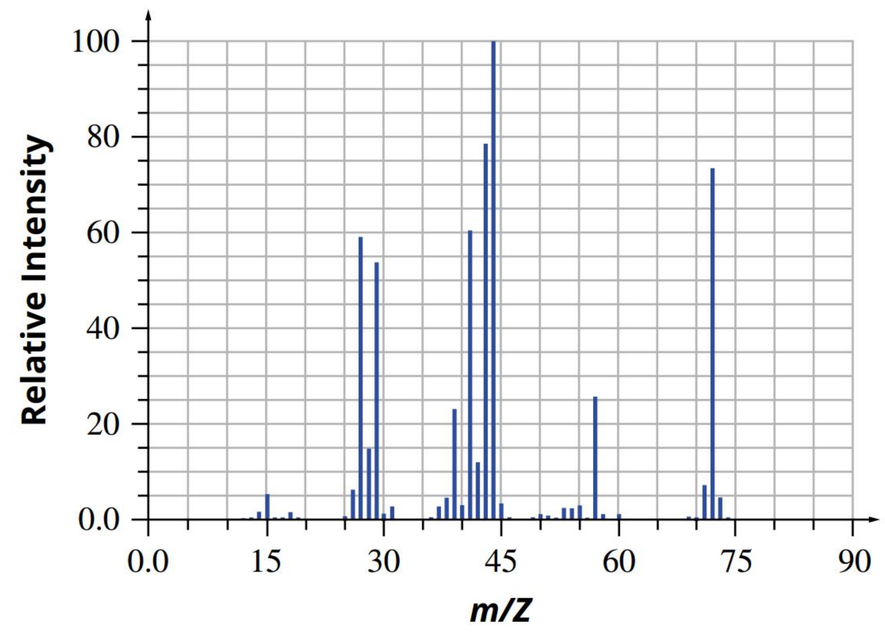


Continued over page

11.5 Review *continued*

7 Identify a compound commonly used in the food industry using the percentage composition data and IR spectra below. Chemical analysis: C: 66.63%, H: 11.18%, O: 22.19%





8 Consider the molecule but-1-ene.

a Predict the key bonds and the wavenumber ranges where you would expect to observe absorption bands on an IR spectrum.

b Predict three different fragments you would expect to observe on a mass spectrum.

Chapter review

11

KEY TERMS

absorption
adsorption
absorption band
amphoteric
base peak
chromatogram
chromatography
components
desorption
electromagnetic spectrum
electrophoresis
fingerprint region
fragmentation
infrared (IR) spectroscopy
isoelectric point
mass spectrometer
mass spectrometry
mass spectrum
mobile phase
molecular ion
molecular ion peak
origin
paper chromatography
polarity
polyacrylamide gel (PAGE)
qualitative analysis
relative intensity
retardation factor (R_f)
solvent front
stationary phase
thin-layer chromatography (TLC)
transmittance
wavenumber

KEY QUESTIONS

Describe

1 In the molecular mass spectrum of an organic compound, the signal produced by the unfragmented molecular ion and the signal produced by the most abundant particle correspond, respectively, to the:

A main ion peak and base peak
B parent (molecular) ion peak and base peak
C base peak and parent (molecular) ion peak
D parent (molecular) ion peak and main ion peak.

2 Define each of the following terms.

a adsorption
b thin-layer chromatography
c desorption

3 State the absorption bands in an infrared spectrum that are used to indicate the presence of:

a an alkene
b an aldehyde.

4 Explain the difference, in terms of amino acids, between the zwitterion and the isoelectric point.

5 Identify the analysis technique that would be preferred when:

a determining the molar mass of a compound
b differentiating between compounds with different functional groups
c differentiating between compounds with the same functional group but different molecular masses.

6 The following table shows the steps in preparing electrophoresis using gel to separate out amino acids. Number the steps in the correct order.

Step	Number
Any neutral amino acids remain stationary in the centre wells.	
Each amino acid sample or known standard is loaded into one of the wells within the gel.	
The gel is placed in an electrophoresis bath where it is covered with a controlled pH solution (buffer) that contains ions to conduct an electric current.	
A power source is attached to the electrophoresis bath and switched on. The electrical current causes the negatively charged amino acids to migrate through the gel towards the positive terminal of the chamber. The positively charged amino acids migrate through the gel towards the negative terminal.	
The colourless amino acids are detected by applying ninhydrin.	
The gel is placed into a gel electrophoresis chamber with the wells situated at the centre of the chamber.	
The electrophoresis gel is prepared. The gel is rectangular and contains small wells (holes) in the centre.	

Apply

7 A sample containing three amino acids, A, B and C, is separated by TLC. The stationary phase is the polar silica gel, and the mobile phase is 100% ethanol. The three amino acids have the following properties.

- Solubility in ethanol: C is much more soluble than A and B. A and B are equally soluble.
- Adsorption to the stationary phase: B is more strongly absorbed than A. C is least strongly adsorbed.

Identify which of the following lists shows the retardation factor (R_f) values of the three amino acids, from lowest to highest.

A A, B, C
B B, A, C
C C, A, B
D C, B, A

8 Select from the following list the amino acid that is non-polar.

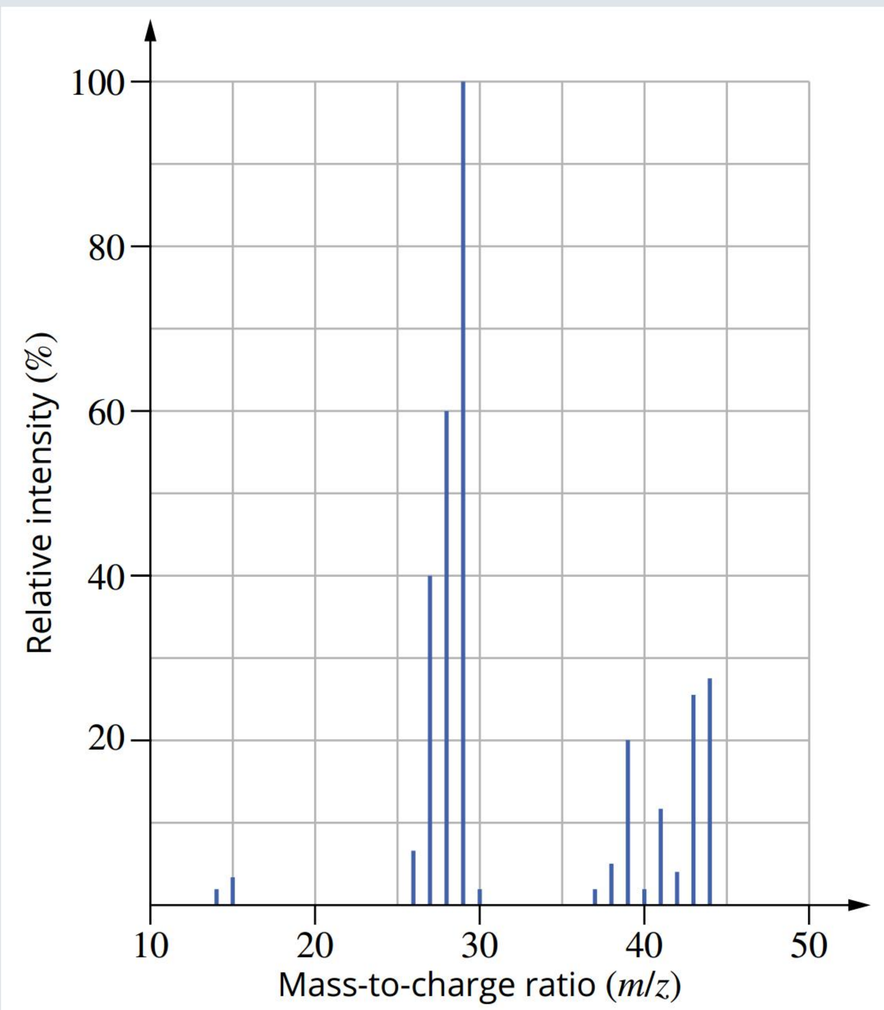
A histidine
B serine
C methionine
D lysine

9 More energy is required to vibrate:

A C–C compared to C=C
B C–O compared to C–H
C C=C compared to C≡C
D C–Cl compared to C–Br.

10 Using Table 11.4.3 on page 487, list the bonds in 2-bromoethan-1-ol in order from the bond that will absorb the lowest energy infrared radiation to the bond that will absorb the highest energy infrared radiation.

11 The mass spectrum of an alkane is shown in the following figure. Identify the formulas of the molecular and base ions.



12 Name the electrode that the amino acid will travel to in electrophoresis when the pH is greater than the isoelectric point.

Analyse

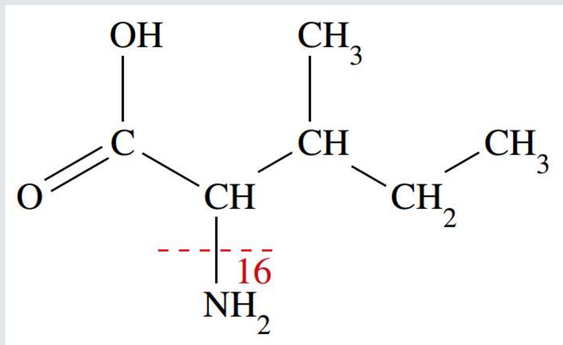
13 Explain how each of the techniques of IR spectroscopy, mass spectrometry, electrophoresis and TLC can be used in the identification of an organic molecule.

14 Calculate the empirical formula of an unknown compound that is 55.14% carbon, 10.42% hydrogen, 16.08% nitrogen and 18.36% oxygen.

15 An unknown compound has a molecular formula of C_3H_6O. Its IR spectrum has a strong, sharp absorption at 1700–1750 cm^{-1}. Identify the possible compounds that could give this absorption band.

16 A scientist has an unknown amino acid sample and wants to identify it using electrophoresis. They test three different pH buffers. At pH 3, the unknown remains stationary. At pH 6 and 9, the amino acid travels to the anode. Determine the identity of the unknown amino acid.

17 The following diagram shows the structure of the amino acid isoleucine.



a State its molecular formula.
b Calculate its molecular mass.
c Identify the chiral centres by marking them with an asterisk (*).
d The mass spectrum of isoleucine includes a signal at $m/z = 16$. The dotted line shows how cleavage might occur to produce the $[NH_2]^+$ fragment that would account for this signal.
For each of the following m/z values from the spectrum of isoleucine, write the formula of the fragment ion likely to be responsible and add a dotted line to your diagram to show a simple bond cleavage that could produce this fragment ion.
i $m/z = 15$
ii $m/z = 29$
iii $m/z = 57$
e The base peak in the mass spectrum is at $m/z = 86$.
i Explain what is meant by the 'base peak' in a mass spectrum.
ii Suggest the fragment that has been lost from the molecular ion to produce the ion responsible for the base peak.